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# Thermodynamic Behavior of Alkanes In Superacid Media

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## I. Introduction

The study of the behavior of saturated hydrocarbons in highly acidic media led to the discovery of their isomerization, observed for the first time in 1902 in the transformation with aluminum chloride of cyclohexane into methylcyclopentane.<sup>1,2</sup> A catalytic cracking with AlCl<sub>3</sub> was described later;<sup>3</sup> subsequently, alkylation reactions have been carried out with AlCl<sub>3</sub>,<sup>4</sup> and in sulfuric acid.<sup>5</sup> These acid-catalyzed transformations of saturated hydrocarbons (fragmentation, alkylation, isomerization) were generally considered to be carbocation reactions involving trivalent carbenium ions.<sup>6-10</sup>

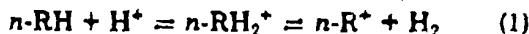
Direct evidence for the existence and structures of alkylcarbenium ions became possible largely through the application of NMR spectroscopy and the use of superacid media.<sup>11,12</sup> The observation of long-lived carbocations has opened a wide field of investigation, first concerning the physicochemical properties of these species and then relative to reactions that can proceed from them.<sup>13-18</sup> In this respect, the catalytic isomerization or alkylation of alkanes, of special interest for the upgrading of motor fuels, may be regarded as one of the most promising applications of superacid media.

TABLE I. Conversion Ratios in the Isomerization of n-Heptane with Different Catalysts

catalyst	working temp. °C	2,2DMBH <sup>a</sup> mole ratio, %
Pt/zeolite	~250	20
Pt/chlorinated alumina	~150	29
AlCl <sub>3</sub> -SbF <sub>5</sub>	~85	36
ShF <sub>3</sub> -HF	~25	53

\* 2,2-Dimethylbutane.

The isomerization of alkanes being slightly exothermic, the reaction is enhanced by a decrease of temperature. Table I shows that the superacid catalyst (HF + SbF<sub>5</sub>) leads to higher ratios of conversion than the conventional processes. In superacid media, the isomerization process is represented as follows:



The initial step (reaction 1) is an oxidation process by H<sup>+</sup> ion into the carbenium ion n-R<sup>+</sup> through a pentacoordinated carbonium n-RH<sub>2</sub><sup>+</sup> resulting from the basic nature of n-RH. The existence of such species has not been proved by spectroscopic methods, but the participation in the process of a three-center bound pentacoordinated carbonium ion raised a controversy<sup>17-21</sup> that we shall not enter. The carbenium ion n-R<sup>+</sup> is rearranged into the more stable ion i-R<sup>+</sup> (branched cation), which is reduced by hydrogen or the excess of alkane n-RH. After an induction period, corresponding to the saturation of the acid phase by carbenium ions, the process is catalytic.

In practice, the overall reaction is not so simple; side reactions, such as condensation, cracking, or alkylation, are observed. From the amount of data published on the chemistry of alkanes in superacid media, the acidity level of the solvent appears to be a major parameter in the orientation of the different reactions. As the acidity levels of the various superacid media present differences that can affect the reactions, it is of prime importance to establish a quantitative scale of these levels;<sup>22</sup> this is the subject of section II.

Recent studies have shown the influence of the acidity level on the reactivity of two hydrocarbons in anhydrous hydrogen fluoride-isopentane<sup>23</sup> and -methylcyclopentane.<sup>24</sup> Furthermore, thermochemical data of the redox reactions in which these two compounds are involved have been determined and represented under the form of a potential-acidity diagram that traduces the reactivity of an alkane as a function of the acidity level. Thus, taking into account these results



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Bernard Trémillon was born in France in 1930. He was graduated engineer from the Ecole Supérieure de Physique et Chimie Industrielles de Paris in 1954 and received the Doctorat-ès-Sciences-Physiques degree from the University of Paris in 1959. In 1960 he joined the University of Paris where he is currently professor of analytical chemistry and director of the doctoral teaching in this area. He is also professor of electrochemistry at the Ecole Nationale Supérieure de Chimie de Paris, where he serves as head of a teaching department and director of the research laboratory entitled "Analytical and Applied Electrochemistry" (associated to C.N.R.S.). His research interests have centered chiefly on chemistry in nonaqueous solvents and in molten salts. He has published about 150 research and review papers and is author or coauthor (with Prof. G. Charlot) of five books.

and thermochemical data from literature, it is possible to calculate the thermochemical properties of any alkane and to describe, from the thermodynamic point of view, its reactivity as a function of the acidity level of the solvent.<sup>24</sup> This is realized for alkanes from methane to hexanes; then the comparison between experimental results and thermochemical previsions is widely discussed and conditions (choice of a medium) for alkylation or isomerization reactions are deduced.

## II. Superacid Media

The most acidic media known are made up by dissolving strong Lewis acids, such as  $\text{BF}_3$ ,  $\text{TaF}_6$ , or  $\text{SbF}_5$ , in solvents that are strong Bronsted acids, such as hydrogen fluoride, sulfuric acid, fluorosulfuric acid, or perfluoroalkanesulfonic acid; these solutions are currently referred to as "superacid media", according to a designation introduced by Gillespie, who has assigned it to any solution in which the activity of  $\text{H}^+$  ion is greater than it is in pure sulfuric acid.<sup>25</sup>

### A. Acidity Scale of the Solvent

The superacid media being made up with a protonic acid HS as a solvent, the acid-base properties are related to the autoprotolysis equilibrium of HS. We present the acidity scale in anhydrous hydrogen fluoride; the results are easily transferred to other solvents. In HF, the autoprotolysis equilibrium is represented as

$$\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^- \quad (4)$$

where  $\text{H}^+$  and  $\text{F}^-$  represent the solvated species.

The acidity of the medium ( $\text{H}^+$  activity,  $a_{\text{H}^+}$ ) is defined by the thermodynamical standard unit.

$$\text{pH} = -\log a_{\text{H}^+}$$

The acidity parameter is reduced to

$$\text{pH} = -\log [\text{H}^+]$$

in the same way as aqueous solutions in diluted ones,<sup>27-29</sup> and related to the autoprotolysis constant  $K_1$  of equilibrium 4 as follows:

$$K_1 = [\text{H}^+][\text{F}^-]$$

or

$$\text{pH} + \text{pF} = \text{p}K_1$$

The value of  $\text{p}K_1$  ( $= -\log K_1$ ) determines the length of the acidity scale of diluted solutions;  $\text{pH} = 0$  corresponds to a 1 M solution of a strong acid ( $[\text{H}^+] = 1 \text{ M}$ ), and  $\text{pH} = \text{p}K_1$  corresponds to a 1 M solution of a strong base ( $[\text{F}^-] = 1 \text{ M}$ ).

The autoprotolysis constants of the different solvents HS have been determined by various methods: conductimetric measurements,<sup>30-35</sup> acidity function determinations,<sup>36-39</sup> or potentiometric titrations.<sup>40-42</sup> The more reliable values are reported in Table II; among the different solvents, hydrogen fluoride presents the widest acidity scale (nearly 14 units), which represents a large variation of the  $\text{H}^+$  ion activity by a factor of about  $10^{14}$  from basic media ( $[\text{F}^-] = 1 \text{ M}$ ) up to acid media ( $[\text{H}^+] = 1 \text{ M}$ ).

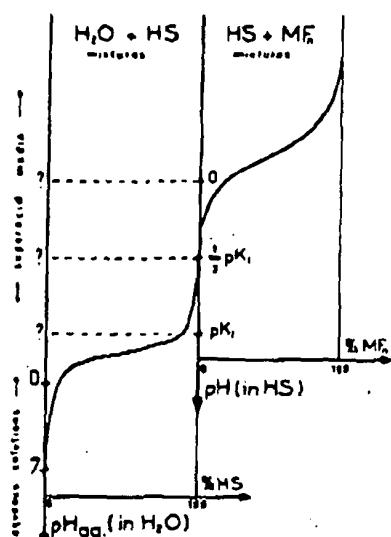
It stands to reason that the  $\text{H}^+$  ion activity variations are not restricted to the acidity scale. There is a continuous increase of  $\text{H}^+$  ion activity from aqueous solutions up to superacid mixtures (HS + MF<sub>n</sub>) through the

## Thermodynamic Behavior of Alkanes

TABLE II. Acidity Properties of Various Solvents  
for Superacid Media<sup>a</sup>

superacid media	pK <sub>1</sub>	H	R <sub>d</sub> (H)
HF, [H <sup>+</sup> ] = 1 M, pH 0 neat	13.7	- 20.5	- 27.9
[KF] = 1 M, pH = pK <sub>1</sub>		- 11.0	- 21.1
HSO <sub>3</sub> F, [H <sup>+</sup> ] = 1 M, pH 0 neat	7.4	- 8.4	- 14.2
[SO <sub>3</sub> F <sup>-</sup> ] = 1 M, pH = pK <sub>1</sub>		- 19.4	
H <sub>2</sub> SO <sub>4</sub> , [H <sup>+</sup> ] = 1 M, pH = 0 neat	3.6	- 15.0	
[HSO <sub>4</sub> <sup>-</sup> ] = 1 M, pH = pK <sub>1</sub>		- 11.5	
CF <sub>3</sub> SO <sub>3</sub> H (neat)	?	- 14.0	
C <sub>6</sub> F <sub>5</sub> SO <sub>3</sub> H (neat)	?	- 18.4	
C <sub>6</sub> F <sub>5</sub> SO <sub>3</sub> H-SbF <sub>5</sub> (10% mol)			

$\text{PK}_1$  ( $\equiv -\log K_1$ ) autoprotolysis constant.



**Figure 1.** Schematic diagram of the acidity increase from aqueous solutions up to superacid mixtures.

$\text{H}_2\text{O} + \text{HS}$  mixtures and then HS solvent (Figure 1).

In order to analyze the reactions, a pH measure that is independent of the solvent but related to the composition of the media is needed. The acidity is then thermodynamically defined according to the relation between the chemical potential  $\mu_{\text{H}^+}$  and the activity  $a_{\text{H}^+}$ :

$$pH = -\log a_{H^+} = \frac{\mu^\circ_{H^+} - \mu_{H^+}}{2.3RT}$$

where pH = 0 corresponds to the reference state (in general aqueous solutions).

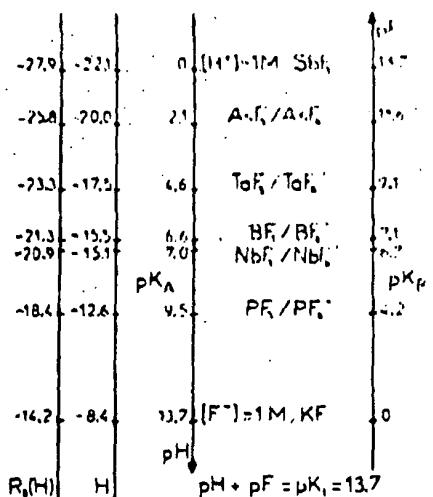
In practice, experimental measurements lead only to approximations of pH through the acidity functions (see section II B).

The acid character of the solvents HS enhances the basicity of a great number of compounds that are weak bases in water. In contrast, it is difficult to find strong acids in HS because of its low basicity. Inorganic acids, such as HCl or  $\text{HClO}_4$ , which are strong acids in water, behave in HS as levants as weak acids.<sup>43</sup> The strongest acids are Lewis acids, such as  $\text{SbF}_5$  and  $\text{TaF}_5$ , according to the acid-base equilibrium 5:



characterized by the acidity constant

$$K_A = \frac{a_H \cdot a_{MP_{n+1}}}{a_{MP}}$$



**Figure 2.** Acidity scale in anhydrous hydrogen fluoride:  $pK_A = -\log [H^+][MF_{n+1}]/[MF_n]$  ( $\approx pK_1 - pK_R$ ). The acidity scale has been placed against the acidity functions  $H$  and  $R_0(H)$  (see section IIB).

The determination of the strength of the Lewis acids  $MF_n$ , has been carried out in the different solvents HS. Numerous techniques have been applied: conductivity measurements,<sup>30,44-51</sup> cryoscopy,<sup>49,60</sup> aromatic hydrocarbons extraction,<sup>52,53</sup> solubility measurements,<sup>54-56</sup> kinetic parameters determinations,<sup>57-60</sup> electroanalytical techniques (hydrogen electrode),<sup>41,60-62</sup> quinones systems as pH indicators,<sup>22,40,43,63</sup> or other electrochemical systems,<sup>64,65</sup> and acidity function  $H_0$  determinations, with UV-visible spectroscopy<sup>38-40,44,66-69</sup> or with NMR spectroscopy.<sup>70-73</sup> The results were somewhat contradictory, but the order of the strength is now well established. The acidity scale in anhydrous hydrogen fluoride is presented in Figure 2, with the acidity constants of various Lewis acids allowed to buffer the medium to a pH value equal to

$$pH = pK_A - \log \frac{a_{MF_n}}{a_{MF_{n+1}}} \quad (pK_A = -\log K_A)$$

or in diluted solutions  $\text{pH} = \text{p}K_A - \log [\text{MF}_n]/[\text{MF}_{n+1}]$ .

In hydrogen fluoride, the strength of the acids is decreasing in the order  $\text{SbF}_5 > \text{AsF}_5 > \text{TaF}_5 > \text{BF}_3 > \text{NbF}_5$ .

### B. General Acidity Scale

A complete interpretation of the reactivity of alkanes needs a comparison between the acidity levels of the various superacid media. The general way is to translate the  $H^+$  ion activity into  $pH_{aq}$ , which is a universal unit (Figure 1). Then, we can consider as an absolute acidity scale the chemical potential scale  $\mu^\circ_{H^+}(HS)$  of  $H^+$  ion (whatever the solvent is); the origin of the scale will be the standard chemical potential of  $H^+$  in water  $\mu^\circ_{H^+}(aq)$ .<sup>27,28</sup> The value  $\mu^\circ_{H^+}(HS) - \mu^\circ_{H^+}(aq)$  is equal to the free energy of  $H^+$  ion transfer from the solvent HS to water:

$$\Delta G_f^{\text{HS}} = \mu^\circ_{\text{H}_2(\text{HS})} - \mu^\circ_{\text{H}_2(\text{aq})} = 2.3RT \log \Gamma_{\text{H}_2(\text{HS})}$$

where  $\Gamma_{H^+}(HS)$  represents the activity coefficient of  $H^+$  transfer.

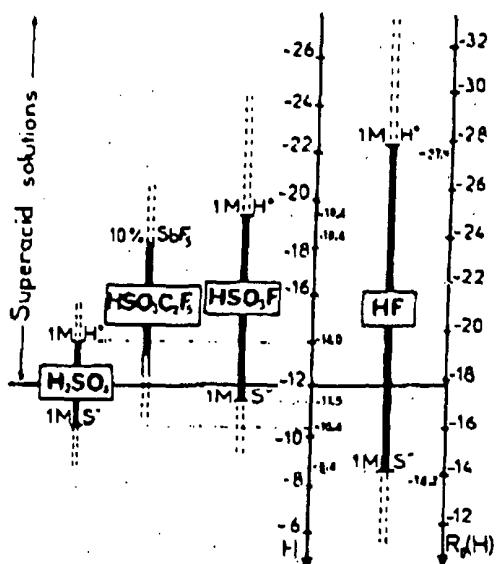


Figure 3. General acidity scale of the various superacid media (the acidity domains ( $pK_i$ ) are represented by full lines).

According to this definition, a solution in HS whose acidity is equal to pH(HS) corresponds to an absolute acidity value,  $pH_{eq}$ , equal to

$$pH_{eq} = pH(HS) - \log \Gamma_{H^+}(HS)$$

As mentioned above, the experimental measurements lead only to approximations of  $pH_{eq}$  in the different solvents. Two principal methods have been developed whose characteristics have been widely discussed:<sup>29,74,75</sup> the Hammett acidity function  $H^{76,77}$  and the Strehlow redox acidity function  $R_0(H)$ .<sup>78-80</sup>

The Hammett acidity functions in the various superacid media are well-known.<sup>38-59,44,86-73,81</sup> The  $H$  values of neat solvents and the values of the limits of the acidity domains ( $[H^+] = 1 M$  and  $[S^-] = 1 M$ ) are reported in Table II, except for the perfluoroalkane-sulfonic acids, whose autoprotolysis constants are not known.<sup>81</sup>

The acidity domains of the different solvents HS are represented by full lines in Figure 3. If we assume that the  $H$  function represents the  $H^+$  activity in HS, the  $H$  value of a molar acidic solution ( $pH(HS) = 0$ ) is calculated by the relation

$$H(pH(HS) = 0) = H(pH(HS) - pK_i(HS)) - pK_i(HS)$$

$H(pH(HS) = pK_i(HS))$  corresponding to a molar basic solution in HS ( $[S^-] = 1 M$ ).

Therefore, the value of the neat solvent is evaluated in the same manner:

$$H(neat HS) = H(pH(HS) - pK_i(HS)) - 0.5pK_i(HS)$$

The differences between calculated and experimental  $H$  values may be attributed for the  $H_0$  value of the neat solvent to the difficulties to get perfectly neat solvents (without  $H_2O$ , which is a strong base in these media) and for the acidic media to the method that requires a set of indicators (whose number increases with the value of  $pK_i$ ) and the assumption on the equality of the indicators activity coefficients.

The Strehlow redox function  $R_0(H)$  affords a simple means of the  $H^+$  activity at any acid concentration from two emf measurements, in contrast to the laborious

indicator procedure. Few data have been reported in literature on the determination of this redox function.  $R_0(H)$  functions have been determined in  $H_2O-H_2SO_4$ <sup>74,82,83</sup> or  $R_0SO_3H$ <sup>84</sup> and in basic or slightly acidic hydrogen fluoride.<sup>40,43,51</sup>

In Figure 3, the  $R_0(H)$ -acidity scale has been placed against the  $H$  acidity scale with respect to the values of the  $H$  and  $R_0(H)$  functions in a molar basic solution in hydrogen fluoride; that is:

$$H(HF, KF 1 M) = -8.4 \text{ (ref 66)}$$

$$R_0(H)(HF, KF 1 M) = -14.2 \text{ (ref 40, 43)}$$

Then, the values of  $H$  functions are translated into  $R_0(H)$  functions:  $R_0(H) = H - 5.8$ . When the same procedure as above is used, the  $R_0(H)$  values are calculated, whatever the acidity level, according to

$$R_0(H)(pH(HS)) = R_0(H)(pH(HS) = 0) + pH(HS)$$

Figure 3 shows the great interest of the media derived from hydrogen fluoride: first, its acidity range covers the acidity ranges of the other systems; second, it provides acidity levels which can be held to be the highest protonic levels (the use of highly concentrated  $SbF_5$  mixtures or neat  $SbF_5$  affords very high acidity levels up to  $H_0 \approx -26$ <sup>73</sup> ( $R_0(H) \approx -32$ ), and third, the oxidizing action of  $SO_3$  has not to be considered (see section II C).

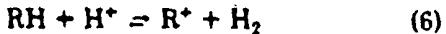
It can be seen that the acidity of superacid media runs from  $H_0 \approx -12$  ( $R_0(H) \approx -18$ ) up to  $H_0 < -22$  ( $R_0(H) < -28$ ); such highly negative values attest the exceedingly weak solvation energy of  $H^+$  ion. Furthermore, the Gibbs free energy  $H^+$  ion in any medium may be evaluated with respect to the free energy  $H^+$  ion formation in water<sup>85-88</sup> according to the relation defined above:

$$\Delta G_f^{HS} = 2.3RT \log \Gamma_{H^+}(HS)$$

Hence, in hydrogen fluoride, if we assume on one hand that the  $H$  function represents  $-\log \Gamma_{H^+}(HS)$ , transfer from water involves a change of about 29 units, which leads to a value of  $\Delta G_f(H^+) \approx 137 \text{ kcal mol}^{-1}$ ; on the other hand, if the  $R_0(H)$  function represents  $-\log \Gamma_{H^+}(HS)$ , transfer from water involves a change of about 35 units, which leads to a value of  $\Delta G_f(H^+) \approx 144 \text{ kcal mol}^{-1}$ .

### C. Oxidizing Power of Superacid Media

Since the first paper reported on the formation of alkylcarbenium ions from alkanes,<sup>12</sup> according to the redox reaction



the claim that alkanes reacted by protonation followed by loss of hydrogen was clouded by the fact that the necessary quantity of  $H_2$  was not always observed. It was suggested that other oxidizing agents must participate to the oxidation of alkanes. Larsen<sup>89</sup> proposed a thermochemical analysis of various oxidation processes according to superacid media.

In the superacid media derived from  $HSO_3F$ , the reduction of  $HSO_3F$  by hydrogen is exothermic<sup>90</sup> and thus may occur. Furthermore, the oxidation of alkanes in  $HSO_3F$  by  $SO_3$  has been shown;<sup>90-92</sup>  $SO_3$  is produced by the dissociation of  $HSO_3F$  into  $HF$  and  $SO_3$ ,<sup>93</sup> the overall oxidation process being



In the mixtures  $HSO_3F + SbF_5$ ,  $SbF_5$  participates in the oxidation of alkanes<sup>24</sup> as was earlier observed in the oxidation of hydrocarbons by  $SbCl_5$ .<sup>95</sup>

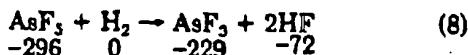
In sulfuric acid, it has been established much earlier than the formation of carbenium ions from alkanes proceeds via the reduction of sulfuric acid into  $SO_2$ .<sup>96,97</sup>

In the media derived from hydrogen fluoride, the standard potential of the redox couple  $H^+/H_2$  has been determined by the use of a hydrogen electrode:<sup>22,20</sup>

$$E^\circ(H^+/H_2) = 0.226 \text{ V} (P_{H_2} = 1 \text{ atm})$$

(potentials are measured vs. the  $Ag/AgSbF_6$  reference electrode<sup>64</sup>). It was also established that  $AsF_5$  is a stronger oxidant than  $H^+$  ion; indeed, in  $SbF_5$  solutions,  $AsF_5$  is slowly reduced by hydrogen (at  $0^\circ\text{C}$  under atmospheric pressure) into  $AsF_3$  while in basic media, where the predominating form of  $AsF_5$  is  $AsF_6^-$ , reduction is not observed (or too slow to be noticeable).<sup>22,60</sup>

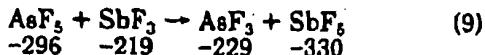
If the procedure of Larsen<sup>98</sup> is followed and one takes into account the formation enthalpies of the compounds,<sup>98-100</sup> the reduction of  $AsF_5$  by  $H_2$  is found to be highly exothermic (the solvation enthalpies are neglected):



$$\Delta H_\theta = -77 \text{ kcal mol}^{-1}$$

In fact, taking into account the electrochemical reduction potential of  $AsF_5$  and the standard redox potential of  $H^+/H_2$ , the free energy of reaction 8 is found to be about  $-5 \text{ kcal mol}^{-1}$ . Thus, in such thermodynamical calculations, the solvation terms must not be neglected.

If we apply Larsen's procedure to the symmetrical reaction 9 in which solvation terms may cancel out  $AsF_5$ ,

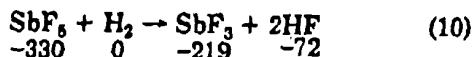


$$\Delta H_\theta = -44 \text{ kcal mol}^{-1}$$

is found to be a higher oxidant than  $SbF_5$ .

With respect to the oxidizing power of  $SbF_5$ , the results are somewhat contradictory. An electrochemical study of the antimony system in HF did not lead to the standard potential of the redox couples because the electrochemical systems are irreversible.<sup>101</sup>

By application of classical thermodynamics, Larsen<sup>98</sup> calculated that the reduction of  $SbF_5$  by  $H_2$  is nicely exothermic:

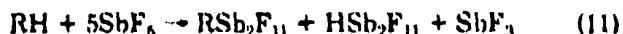


$$\Delta H_{10} = -33 \text{ kcal mol}^{-1}$$

The calculated value of  $\Delta H_{10}$  does not afford a definitive conclusion  $SbF_5$  being a weaker oxidant than  $AsF_5$  and taking into account the difference between calculations and experimental estimations.

The oxidation of alkanes or hydrogen by  $SbF_5$  has been observed in various experiments:<sup>98,102-105</sup> hydrogen is oxidized by  $SbF_5$  at room temperature under high pressure,  $P_{H_2} = 50 \text{ atm}$ ;<sup>102-104</sup> in highly concentrated solutions of  $SbF_5$ , neat  $SbF_5$ , or  $SbF_5$  in  $SO_2$  or  $SO_2ClF$ ,

alkanes are oxidized by  $SbF_5$  according to reaction 11.<sup>104</sup>



This reaction, suggested in the oxidation of methane, would be followed in the oxidation of isobutane by



In contrast, it has been shown that hydrogen is not oxidized by  $SbF_5$  diluted in HF or  $HSO_3F$ .<sup>101,103-105</sup> Furthermore, a polarographic determination of  $SbF_5$ <sup>106</sup> in  $HF + SbF_5$  mixtures ( $SbF_5$  up to 4 M), in which *n*-pentane was previously isomerized under hydrogen pressure, did not lead to evidence for  $SbF_5$  reduction in the process.<sup>110</sup>

The oxidizing power of  $SbF_5$  is still ill-defined,  $SbF_5$  behaving as a strong acid in diluted solutions; its predominating form is  $SbF_6^-$ .<sup>54</sup> Thus, as for  $AsF_5$ , the reduction of the anionic form may not occur (or is too slow), while in concentrated solutions or in neat  $SbF_5$ , free  $SbF_5$  (or polymerized forms  $Sb_nF_{5n+1}$ )<sup>44,46,111,112</sup> may be slowly reduced by hydrogen or alkanes. However, if the oxidizing power of  $SbF_5$  is not well established, one can see that the media derived from hydrogen fluoride offer the advantage over other media that the oxidizing action of  $SO_3$  does not have to be considered. In the following sections, we shall consider that  $H^+$  ion is the principal oxidant of alkanes.

### III. Establishment of the Thermochemical Properties of Alkanes

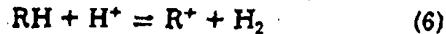
The acidity range in superacid media runs from an  $H$  value of  $-12$  to  $-26$  (see section IIIB), which means an increase of the  $H^+$  activity of  $10^{14}$  from the lower limit up to the higher one. Such an increase must change the redox properties of alkanes in these media; this is confirmed by studies of the chemical behavior of isopentane<sup>23</sup> and methylcyclopentane<sup>24</sup> in hydrogen fluoride. The reactivity of these two compounds is represented under the form of a potential acidity diagram (Pourbaix's type).

#### A. General Representation of Alkane Reactivity

The in situ determination of alkane concentration, by electrochemical methods, allowed quantitative analysis of the reactions in which the two hydrocarbons are involved. Different reactions were observed according to the acidity level, and their equilibrium constants were determined.<sup>23,24</sup>

##### 1. Oxidation of RH into Carbenium Ion R<sup>+</sup>

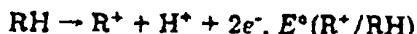
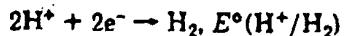
As expected, isopentane and methylcyclopentane undergo chemical oxidation by  $H^+$  ion in acidic HF:



characterized by the constant  $K_R$ :

$$K_R = \frac{[R^+]P_{H_2}}{[RH][H^+]} = R_R \frac{P_{H_2}}{[H^+]}$$

The oxidation process is the sum of the two electrochemical reactions:



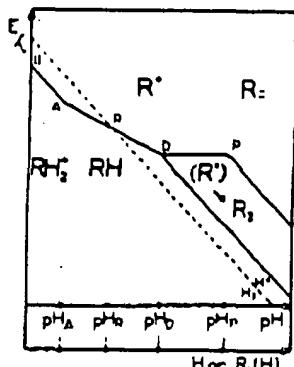


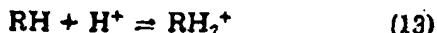
Figure 4. General potential-acidity diagram of an alkane RH in hydrogen fluoride. The potential-acidity diagram of RH (full lines) is placed against the  $\text{H}^+/\text{H}_2$  system (dashed line).

Therefore, the constant  $K_R$  is related to the standard potentials of the redox couples  $\text{R}^+/\text{RH}$  and  $\text{H}^+/\text{H}_2$  according to

$$\frac{2.3RT}{2F} \log K_R = E^\circ(\text{H}^+/\text{H}_2) - E^\circ(\text{R}^+/\text{RH})$$

The experimental determination of the ratio  $R_R$  led to the calculation of  $K_R$  and  $E^\circ(\text{R}^+/\text{RH})$ , which allows one to plot the part B-D of the potential-acidity diagram (Figure 4) vs. the  $\text{H}^+/\text{H}_2$  system.<sup>22,23</sup> The ensuing crossing ( $\text{pH}_R = \log K_R$ ) of the two lines representing the  $\text{H}^+/\text{H}_2$  and  $\text{R}^+/\text{RH}$  systems means that spontaneous oxidation of RH into  $\text{R}^+$  runs almost to completeness at pH values lower than  $\text{pH}_R$  and no longer takes place when the acidity level is too low ( $\text{pH} > \text{pH}_R$ ).

In  $\text{SbF}_6$  solutions, the ratio  $R_R$  becomes independent of pH. This means that the oxidation process does not imply the  $\text{H}^+$  ion; that is to say that RH is protonated into the carbonium ion, as follows:



which liberates  $\text{H}_2$  to yield the carbonium ion  $\text{R}^+$ .

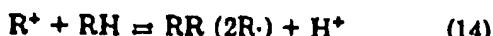
Reaction 13 renders an account of the basic nature of RH; point A represents the acidity level of RH protonation:

$$\text{pH}_A = \text{p}K_A (-\log K_A) = \log \frac{[\text{RH}_2^+]}{[\text{RH}][\text{H}^+]}$$

where  $K_A$  is the acidity constant of  $\text{RH}_2^+$ .

## 2. Alkylation of RH by $\text{R}^+$

In basic media, a different behavior has been observed: the addition of  $\text{R}^+$  to a RH solution produces a decrease of the RH concentration. This is interpreted by the production of a redox reaction between  $\text{R}^+$  (oxidation state +II) and RH (oxidation state 0), yielding the radical oxidation state (+I,  $\text{R}\cdot$ ), which gives at first a dimer RR and then polymeric species, as follows:



Then



or

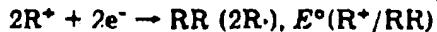


TABLE III. Characteristics of Potential-Acidity Diagrams<sup>a</sup> of Isopentane<sup>b</sup> and Methylcyclopentane<sup>c</sup> in HF (at 0 °C)

alkane, RH	A $\text{RH}_2^+/\text{RH}$	R $\text{R}^+/\text{RH}$	D $\text{RR}/\text{R}^+, \text{RH}$	P $\text{R}^+/\text{R}$
i-C <sub>5</sub> H <sub>12</sub> pH (HF)	1.2	2.7	5.7	>13.7
H	-20.9	-19.4	-16.4	>-8.4
$\text{R}_o(\text{H})$	-26.7	-25.2	-22.2	>-14.2
MCPh, pH (HF)	2.3	4.2	8.1	>13.7
H	-19.8	-17.9	-14.0	>-8.4
$\text{R}_o(\text{H})$	-25.6	-23.7	-19.8	>-14.2

<sup>a</sup> Acidity level of protonation of alkane (A), oxidation of alkane into carbonium ion (R), disproportionation of the dimer (D), and protonation of alkene (P). The conjugate bases (alkenes) of isopentyl and methylcyclopentyl ions are strong bases.<sup>11,12</sup>

Reaction 14 is the sum of the two electrochemical reactions:



and, therefore, the equilibrium constant  $K_D$  of reaction 14

$$K_D = \frac{[\text{RR}][\text{H}^+]}{[\text{RH}][\text{R}^+]}$$

is related to the standard potentials of the redox couples  $\text{R}^+/\text{RR}$  and  $\text{RR}/\text{RH}$  according to

$$\frac{2.3RT}{2F} \log K_D = E^\circ(\text{R}^+/\text{RR}) - E^\circ(\text{RR}/\text{RH})$$

Thus, the experimental determination of  $K_D$  led to the determination of the standard potentials of these two redox couples and to complete the potential-acidity diagram (Figure 4). The diagram shows the radical oxidation state domain, which is limited on the acid side by  $\text{pH}_D (= -\log K_D)$ . In basic media, alkene ( $\text{R}_o$ ) becomes the predominating form of the  $\text{R}^+$  oxidation state, according to



characterized by the acidity constant  $K_p$ :

$$K_p = \frac{[\text{R}_o][\text{H}^+]}{[\text{R}^+]}$$

The acidity level of alkane protonation is represented by  $\text{pH}_p (= -\log K_p = \text{p}K_p)$ .

The characteristics of the experimental potential-acidity diagrams of isopentane and methylcyclopentane are reported in Table III. The potential-acidity diagram of RH (Figure 4) shows that RH oxidation by  $\text{H}^+$  directly gives the carbocation  $\text{R}^+$ , only in acidity levels higher than  $\text{pH}_D$ ; however, there is an equilibrium between the various species over the whole acidity range ( $\Delta G$ 's are slightly positive for  $\text{pH} > \text{pH}_D$ ). In basic media, the formation of radicals enhances condensation reactions that can be followed by polymerization or cracking.

Such a potential-acidity diagram, which represents the variation of redox properties of hydrocarbon with acidity, should be established for other alkanes. In fact, most of them did not appear susceptible to the same

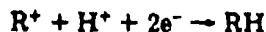
## Thermodynamic Behavior of Alkanes

experimental determinations because of side reactions: isomerization or high reactivity of the carbenium ions. Nevertheless, it is possible to calculate their equilibrium characteristics by estimating the differences between them and those pertaining to isopentane.

### B. Standard Potentials of Redox Couples of Alkanes

The standard potentials of redox couples of alkanes (from methane to hexanes) are calculated at the temperature of 0 °C in HF; the general acidity scale permits transfer of the results in the other superacid media. The following abbreviations have been used to represent the alkanes: C<sub>1</sub>H, methane; C<sub>2</sub>H, ethane; C<sub>3</sub>H, propane; n-C<sub>4</sub>H, n-butane; i-C<sub>4</sub>H, isobutane; n-C<sub>5</sub>H, n-pentane; i-C<sub>5</sub>H, isopentane; neo-C<sub>5</sub>H, neopentane; n-C<sub>6</sub>H, n-hexane; 2MPH, 2-methylpentane; 3MPH, 3-methylpentane; 22DMBH, 2,2-dimethylbutane; 23DMBH, 2,3-dimethylbutane.

The redox couples of alkanes that we consider are

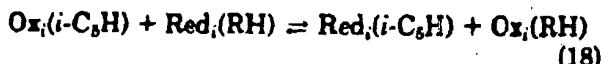


and represented by the general electrochemical reaction



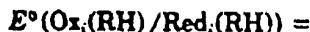
which is characterized by the standard potential E°(Ox<sub>i</sub>(RH)/Red<sub>i</sub>(RH)).

The procedure is to calculate the Gibbs free energies of the redox reactions between the redox couples of isopentane, i-C<sub>5</sub>H, (reference alkane), and those of the alkane RH,



where  $\Delta G_i(RH) = \Delta G_{18} = \Delta G_f(Ox_i(RH)) - \Delta G_f(Ox_i(i-C_5H)) - [\Delta G_f(Red_i(RH)) - \Delta G_f(Red_i(i-C_5H))]$ .

From the experimental determination of the standard potentials E°(Ox<sub>i</sub>(i-C<sub>5</sub>H)/Red<sub>i</sub>(i-C<sub>5</sub>H)),<sup>23</sup> the calculation of  $\Delta G_i(RH)$  leads to the determination of the standard potentials E°(Ox<sub>i</sub>(RH)/Red<sub>i</sub>(RH)) according to



$$E^\circ(Ox_i(i-C_5H)/Red_i(i-C_5H)) + \frac{\Delta G_i(RH)}{2F}$$

Such calculations are rigorous if the values of Gibbs free energies take into account the medium in which the reactions take place, either HF or any superacid media, that is, the free energies of solvation of the different species. Unfortunately, these values are not known. Then, we had to make a number of approximations and assumptions, some of which are open to just criticism. However, taking into account the symmetry of reaction 18, the calculations are based on the following hypothesis:<sup>25</sup> (i) the equality of the solvation energies of the different alkanes on one hand and those of the different alkenes on the other was admitted; (ii) the evaluation of the solvation energies of the carbocations ions was made according to a model of electrostatic interactions, developed by Franklin.<sup>115</sup>

The thermochemical properties of alkanes and alkenes are well-known.<sup>116-118</sup> In hydrogen fluoride or

TABLE IV. Relative Gibbs Free Energies of Formation Redox Couples of Alkanes<sup>a,b</sup>

hydrocarbon	RH	alkene, dimer, R-R	carbenium ion, R <sup>+</sup>	alkene R
C <sub>1</sub> H	29.0	62.1	75	
C <sub>2</sub> H	23.8	47.1	49	30.5
C <sub>3</sub> H	16.3	30.7	25	19.8
n-C <sub>4</sub> H	8.7	16.1	19	10.2
i-C <sub>4</sub> H	7.6	15.9	8.4	9.1
n-C <sub>5</sub> H	1.2	2.1	11	2.2
i-C <sub>5</sub> H	0	0	0	0
neo-C <sub>5</sub> H	-1.2	-1.1	28	
n-C <sub>6</sub> H	-6.3	-7.8	3.3	6.0
2MPH	-7.4	-12.9	-7.8	-8.4
3MPH	-6.9	-10.9	-6.6	-7.9
22DMBH	-8.8	-8.4	-3.6	-2.6
23DMBH	-6.5	-8.1	-7.6	-8.1

<sup>a</sup> kcal mol<sup>-1</sup>. <sup>b</sup> The Gibbs free energies of formation of isopentane (reference alkane) redox couples are RH = -59.0, RR = -97.4, R<sup>+</sup> = 101.2, and R<sub>c</sub> = -32.3 kcal mol<sup>-1</sup>.

superacid media, the solubility determinations show that the alkanes solubility is weak and nearly independent of the hydrocarbon net<sup>123</sup>. Thus, we can assume that the solvation energies are equal in the set of the considered hydrocarbons, which is nearly true in water.<sup>124-128</sup> The Gibbs free energies of formation of these species are reported in Table IV.

The thermochemical properties of carbenium ions R<sup>+</sup> are now well established in the gas phase.<sup>129-140</sup> Unfortunately, their solvation energies are not known in hydrogen fluoride or any superacid media. Arnett et al.<sup>141-144</sup> reported calorimetric measurements of ionization of alkyl halides by SBF<sub>5</sub>; the experiments having been carried out in low dissociative solvents (SO<sub>2</sub>, SO<sub>2</sub>ClF...), the effects of solvation are negligible vs. the ones of Brønsted acids (HF, HSO<sub>3</sub>F...). Therefore, the heats of R<sup>+</sup> formation derived from these measurements are of the same order of magnitude as in the gas phase.

A convenient way to evaluate the solvation terms is to proceed by calculation, derived from the Born equation.<sup>115,145,146</sup> The model, proposed by Franklin,<sup>116</sup> of electrostatic interactions leads to the evaluation of the solvation energies in water. We admit that the differences between the solvation terms of R<sup>+</sup> and i-C<sub>5</sub><sup>+</sup> (reference ion) are equal in water and hydrogen fluoride. Despite its easiness to handle,<sup>147</sup> furthermore, in the set of considered cations the delocalization of the positive charge has to be taken into account.<sup>148,149</sup> In fact, as the calculation needs differences of Gibbs free energies of formation between R<sup>+</sup> and i-C<sub>5</sub><sup>+</sup>, this method has been found to be satisfactory for parent cations of i-C<sub>5</sub><sup>+</sup> except for light cations (<C<sub>4</sub><sup>+</sup>), where the solvation terms appeared to be underestimated.<sup>26</sup> Therefore, the solvation energies of these light cations are taken from the values, reported by Jorgenson,<sup>149</sup> derived from molecular orbital calculations. The relative Gibbs free energies of formation of alkyl-carbenium ions are reported in Table IV.

The calculation of the Gibbs free energies of the redox reaction 18 for each redox couple of alkanes leads to the alkanes' standard potential in HF (which means at an acidity level of H = -22.1 or R<sub>0</sub>(H) = -27.9). These values are reported in Table V.

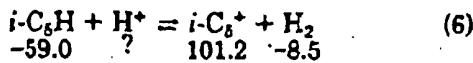
If we apply the calculated Gibbs free energies of formation of isopentane redox couples to the reactions whose constants have been experimentally deter-

TABLE V. Standard Potentials of Redox Couples of Alkanes in Hydrogen Fluoride ( $H$ ) 22.1  
 $R_o(H) = 27.9^a$

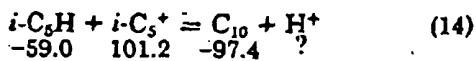
alkane	$E^\circ(R'/RH)$	$E^\circ(R'/RR)$	$E^\circ(RR/RH)$
C <sub>2</sub> H	1.15	1.91	0.40
C <sub>3</sub> H	0.70	1.10	0.30
C <sub>4</sub> H	0.34	0.42	0.27
n-C <sub>5</sub> H	0.38	0.48	0.28
i-C <sub>4</sub> H	0.17	0.02	0.33
n-C <sub>6</sub> H	0.37	0.43	0.30
i-C <sub>5</sub> H	0.15 <sup>b</sup>	0 <sup>b</sup>	0.31 <sup>b</sup>
neo-C <sub>5</sub> H	0.78	1.24	0.34
n-C <sub>7</sub> H	0.36	0.31	0.41
2MPH	0.14	-0.06	0.35
3MPH	0.16	-0.05	0.37
22DMBH	0.26	0.03	0.50
23DMBH	0.13	-0.15	0.41

<sup>a</sup> The potentials (V) are expressed vs. the Ag/AgSbF<sub>6</sub> reference electrode. <sup>b</sup> Experimental standard potentials of isopentane redox couples.<sup>23</sup>

mined,<sup>23</sup> the Gibbs free energy of H<sup>+</sup> ion formation is thus evaluated: On one hand, reaction 6 in HF is exoenergetic ( $\Delta G_6 = -2.3RT \log K_R = -3.4 \text{ kcal mol}^{-1}$ ):



Therefore,  $\Delta G_f(\text{H}^+) \approx 148 \text{ kcal mol}^{-1}$ . On the other hand, reaction 14 in HF is endoenergetic ( $\Delta G_{14} = -2.3RT \log K_D = 7.1 \text{ kcal mol}^{-1}$ ):



Therefore,  $\Delta G_f(\text{H}^+) \approx 145 \text{ kcal mol}^{-1}$ .

Taking into account the hypothesis required in the evaluation of the thermochemical properties of alkanes, one can notice a good agreement between these values and the  $\Delta G_f(\text{H}^+)$  value calculated from the  $R_o(H)$  acidity function. Furthermore, the Gibbs free energies of reaction 6, which are calculated or derived from experimental results, may be compared. Thanks to the above calculations, the difference  $\Delta G_6(i\text{-C}_5\text{H}) - \Delta G_6(i\text{-C}_5^+)$  is found to be equal to 0.8 kcal mol<sup>-1</sup>. Taking into account the equilibrium constant of oxidation of isobutane<sup>160</sup> and that of isopentane,<sup>23</sup> which have been experimentally determined in HF-SbF<sub>5</sub>, the above-mentioned difference is found to be equal to 0.7 kcal mol<sup>-1</sup>. Such a good agreement has been already observed for cycloalkanes where previous thermochemical calculations<sup>24,151</sup> and experimental determinations<sup>24,151</sup> are close.<sup>25</sup>

### C. Acidity Constants of Carbenium Ions, R<sup>+</sup>

Alkylcarbenium ions can be prepared in superacid media by dissolving the corresponding alcohols, alkyl halides, or alkenes.<sup>152-158</sup> The formation of R<sup>+</sup> ions comes from the basic nature of these latter compounds. In less acidic media, the carbenium ion leads to the corresponding alkene by a loss of H<sup>+</sup> ion, according to the acid-base equilibrium represented as follows:



Taking into account the acidity constant of i-C<sub>5</sub><sup>+</sup> reported by Hogeveen et al.<sup>150</sup> and the thermochemical properties of alkenes and carbenium ions, the acidity constant of any carbenium ion is calculated. The Gibbs

TABLE VI. Acidity Constants of Carbenium Ions in Hydrogen Fluoride (pK<sub>P</sub>) and Acidity Levels of Alkene Protonation ( $H_P$  or  $R_o(H_P)$ )<sup>a</sup>

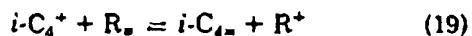
R'/R	pK <sub>P</sub>	H <sub>P</sub>	R <sub>o</sub> (H <sub>P</sub> )
C <sub>2</sub> <sup>+</sup> /C <sub>2</sub>	0.4	21.7	27.5
C <sub>3</sub> <sup>+</sup> /C <sub>3</sub>	11.0 (9.5 <sup>b</sup> )	11.1	16.9
n-C <sub>4</sub> <sup>+</sup> /n-C <sub>4</sub>	8.1	14.0	19.8
i-C <sub>4</sub> <sup>+</sup> /i-C <sub>4</sub>	15.8 <sup>c</sup> (SB <sup>b</sup> )	6.3 (8.5 <sup>c</sup> )	12.1
n-C <sub>5</sub> <sup>+</sup> /n-C <sub>5</sub>	8.2 (8.4 <sup>b</sup> )	13.9	19.7
i-C <sub>5</sub> <sup>+</sup> /i-C <sub>5</sub>	15.2 (SB <sup>b</sup> )	6.9	12.7
n-C <sub>6</sub> <sup>+</sup> /n-C <sub>6</sub>	7.8	14.3	20.1
2MP <sup>+</sup> /2MP	14.7	7.1	13.2
3MP <sup>+</sup> /3MP	14.2	7.9	13.7
22DMBH <sup>+</sup> /22DMBH	16.0	6.1	11.3
23DMBH <sup>+</sup> /23DMBH	14.8	7.3	13.1

<sup>a</sup> Acidity constant reported by Hogeveen et al.<sup>150</sup> when pK<sub>P</sub> > 13.7 (pK<sub>P</sub>(HF)), the alkene is a strong base (SB) in HF.

<sup>b</sup> Experimental values from ref 113 and 114.

<sup>c</sup> From ref 158, 159.

free energy of the acid-base equilibrium 19 is evaluated as follows:



characterized by the constant  $K_{19}$

$$K_{19} = \frac{[i\text{-C}_4^+][\text{R}^+]}{[i\text{-C}_4^+][\text{R}_o]} = \frac{K_P(i\text{-C}_4^+)}{K_P(\text{R}^+)}$$

$\Delta G_{19} =$

$$\Delta G_f(\text{R}^+) - \Delta G_f(i\text{-C}_4^+) - (\Delta G_f(\text{R}_o) - \Delta G_f(i\text{-C}_4))$$

The  $\Delta G_{19}$  value leads to the calculation of pK<sub>P</sub>(R<sup>+</sup>) according to

$$\text{pK}_P(\text{R}^+) = \text{pK}_P(i\text{-C}_4^+) - \frac{\Delta G_{19}}{2.3RT}$$

The values of pK<sub>P</sub>(R<sup>+</sup>) are reported in Table VI.

Linear alkenes, conjugate bases of n-alkylcarbenium ions, behave as weak bases in HF. In contrast, alkenes that are protonated into tertiary carbenium ions behave as strong bases in HF (pK<sub>P</sub>(R<sup>+</sup>) > pK<sub>P</sub>(HF)) or in superacid solvents because the acidity range of HF covers those of the different Brønsted acids (Figure 3). Thus, the latter alkenes are quantitatively protonated into carbenium ions.

From the values of the acidity levels of alkenes protonation (Table VI), one can see that every alkene is protonated in the "superacid" media except ethene, which is protonated only in highly superacid media ( $H < -21$ ), that is, in HF-TaF<sub>5</sub><sup>156,157</sup> or HF-SbF<sub>5</sub> mixtures.<sup>23,113</sup> Recently, acid-base titrations of an acid (SbF<sub>5</sub> or TaF<sub>5</sub>) by alkenes have been carried out in hydrogen fluoride, using quinonic redox systems as pH indicators. Good agreement is found between the calculated values and the determined ones from the titration curves,<sup>113,114</sup> as for the acidity level of alkene protonation in H<sub>2</sub>SO<sub>4</sub><sup>158,159</sup> (see Table VI).

Therefore, if alkene intermediates have been suggested in aqueous H<sub>2</sub>SO<sub>4</sub> or HF to explain alkylation or cracking reactions,<sup>150,161</sup> it is highly probable that in superacid media there will be no alkene formation. In contrast, the basic nature of alkenes is of great interest for hydrocarbon chemistry in superacid media because it provides a convenient preparation of carbenium ion solutions<sup>158</sup> for alkylation processes or isomerization initiations (see following sections).

## Thermodynamic Behavior of Alkanes

TABLE VII. Acidity Constants of Carbonium Ions in HF ( $pK_A$ ) or Acidity Levels of Protonation of Alkanes ( $H_A$  or  $R_0(H)_A$ )

$RH_2^+ / RH$	$pK_A$	$H_A$	$R_0(H)_A$
$C_2H_5^+ / C_2H$	~ 6	~ 28	~ 34
$C_3H_7^+ / C_3H$	~ 5	~ 27	~ 33
$C_4H_9^+ / C_4H$	~ 2	~ 20	~ 26
$i-C_4H_9^+ / i-C_4H$	~ 1	~ 21	~ 27
$i-C_5H_{11}^+ / i-C_5H$	1.2°	20.0	~ 26.7
MCPH <sup>+</sup> / MCPH	2.3°	19.8	~ 25.6

<sup>a</sup> Experimental values from ref 23 and 24.D. Acidity Constants of Carbonium Ions,  $RH_2^+$ 

Because of the high activity of the  $H^+$  ion, the protonation of alkanes<sup>18,20</sup> has been postulated to explain the chemical behavior of these compounds. No spectral evidence for  $RH_2^+$  cations could be given except in the course of gaseous ionic reactions in the source of mass spectrometer.<sup>162,163</sup> The existence in solution of carbonium ions has been shown in studies of the oxidation equilibria of isopentane and methylcyclopentane<sup>23,24</sup> (reaction 13).

Taking into account the recently published values of heats of formation of a few carbonium ions (from methonium ion to isobutonium ion),<sup>164,165</sup> the acidity constants of these cations are estimated. Isopentane and isobutane behaving in the same manner in superacid media,<sup>168</sup> it is admitted that  $K_A(i-C_4H_2^+) \approx K_A(i-C_5H_2^+)$ , which means that  $pK_A(i-C_4H_2^+) \approx 1 (-\log K_A)$ . Thus, the enthalpy of reaction 20 is calculated as follows:



characterized by the constant  $K_{20}$

$$K_{20} = \frac{[RH][i-C_4H_2^+]}{[RH_2^+][i-C_4H]} = \frac{K_A(RH_2^+)}{K_A(i-C_4H_2^+)}$$

$$\Delta H_{20} = \Delta H_f(RH) - \Delta H_f(i-C_4H) - (\Delta H_f(RH_2^+) - \Delta H_f(i-C_4H_2^+))$$

The value of  $\Delta H_{20}$  leads to estimate  $pK_A(RH_2^+)$  according to the relation

$$pK_A(RH_2^+) - pK_A(i-C_4H_2^+) \approx \frac{\Delta H_{20}}{2.3RT}$$

Such calculations should include the solvation heats, which are not known. Thus, as above described, (i) the equality of the solvation terms of the different alkanes and (ii) the equality of the solvation energies between carbonium ions and carbenium ions, which have been estimated previously,<sup>149</sup> are admitted.

The  $pK_A$  values of a few carbonium ions are reported in Table VII.

The basic nature of alkanes explains the augmentation of their solubility when the acidity level is increased.<sup>119,120,166,167</sup> If the solubility is represented as

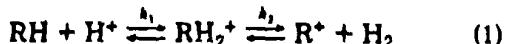
$$S(RH) = [RH] + [RH_2^+] = [RH] \left[ 1 + \frac{[H^+]}{K_A(RH_2^+)} \right]$$

one can see the influence of acidity on the solubility; the application of this relation to *n*-pentane solubility<sup>168</sup> leads to a  $pK_A(n-C_5H_2^+)$  of about 1.1.

According to the  $pK_A(RH_2^+)$  values reported in Table VII, it appears that methane and ethane are very weak

bases. They must not be protonated in the acidity range of HF or in the highest superacid media HF + SbF<sub>5</sub>. This weakly basic nature is confirmed by their electrochemical behavior in HF-SbF<sub>5</sub>.<sup>25,168</sup> When alkanes are protonated, the voltammograms show, by linear sweep voltammetry, oxidation peaks whose characteristics are different from the ones attributed to the unprotonated alkanes. These oxidation peaks, corresponding to the carbonium ions, are observed for any alkane except methane and ethane.<sup>26,164</sup>

The other alkanes are protonated in HF-SbF<sub>5</sub> solutions, which means at acidity levels higher than  $H \sim -20$  or  $R_0(H) \sim -26$ . The question "why has no spectral evidence been given?" may be answered by the kinetic parameters of the oxidation reaction 1:



It has been shown by kinetic analysis that the first reaction (protonation) is the limiting step,  $k_1 << k_2$ .<sup>25,113</sup> Thus,  $RH_2^+$  concentration is always low vs. RH at the beginning of the oxidation or that of  $R^+$  at the end of the process. When equilibrium is reached, the ratio  $RH_2^+/R^+$  is equal to

$$[RH_2^+]/[R^+] = P_{H_2}/28$$

for isopentane<sup>23</sup>  $P_{H_2}$  in atm.

Therefore, in order to get the carbonium ion as the predominating form, the hydrogen pressure must be quite high.

Despite the uncertainties on the  $pK_A(RH_2^+)$  values, the existence of  $RH_2^+$  shall be taken into account in the establishment of the potential-acidity diagrams of alkanes. The  $pK_A$  values of the carbonium ions that could not be calculated are assumed to be of the same magnitude as that of the isopentonium ion:  $pK_A(RH_2^+) \approx 1$  for higher alkanes than butanes.

## E. Potential-Acidity Diagrams of Alkanes

The calculation of the standard potentials of alkanes' redox couples (Table V) leads to the establishment of the potential-acidity diagrams in hydrogen fluoride. If the different species in the various superacid media are solvated in the same manner, these diagrams are easily transposable to any medium through the general acidity scale (Figure 3).

The electrochemical reactions are the following:



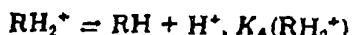
with

$$R^+ \rightleftharpoons R_m + H^+, K_p(R^+)$$

The apparent potential  $E^\circ(R^+/RH)$  is related to the acidity (pH in HF) by

$$E^\circ(R^+/RH) = E^\circ(R^+/RH) - \frac{2.3RT}{2F} pH - \frac{2.3RT}{2F} \log \left( 1 + \frac{K_p(R^+)}{[H^+]} \right)$$

Taking into account the protonation of alkane:



the apparent potential is determined by the relation

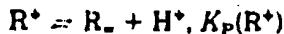
$$E^\circ(R^+/RH) = E^\circ(R^+/RH) - \frac{2.3RT}{2F} \text{pH} - \frac{2.3RT}{2F}$$

$$\log \left( 1 + \frac{K_p(R^+)}{[H^+]} \right) + \frac{2.3RT}{2F} \log \left( 1 + \frac{[H^+]}{K_A(RH_2^+)} \right)$$

The second electrochemical reaction is as follows:



with

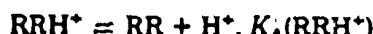


The apparent potential  $E^\circ(R^+/RH)$  is related to the acidity pH in HF by

$$E^\circ(R^+/RR) =$$

$$E^\circ(R^+/RR) - \frac{2.3RT}{F} \log \left( 1 + \frac{K_p(R^+)}{[H^+]} \right)$$

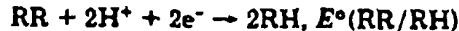
Allowing for the protonation of alkane RR:



the apparent potential is determined according to

$$E^\circ(R^+/RR) = E^\circ(R^+/RR) - \frac{2.3RT}{F} \log \left( 1 + \frac{K_p(R^+)}{[H^+]} \right) + \frac{2.3RT}{2F} \log \left( 1 + \frac{[H^+]}{K_A(RRH^+)} \right)$$

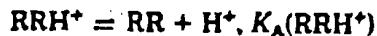
The third electrochemical reaction is as follows:



The apparent potential  $E^\circ(RR/RH)$  is related to the acidity (pH in HF) by

$$E^\circ(RR/RH) = E^\circ(RR/RH) - \frac{2.3RT}{F} \text{pH}$$

Considering the protonation of alkanes RH and RR:

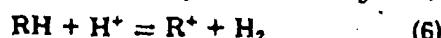


the apparent potential is determined according to

$$E^\circ(RR/RH) - \frac{2.3RT}{F} \text{pH} + \frac{2.3RT}{F} \log \left( 1 + \frac{[H^+]}{K_A(RH_2^+)} \right) - \frac{2.3RT}{2F} \log \left( 1 + \frac{[H^+]}{K_A(RRH^+)} \right)$$

The variations of the redox properties of alkanes as a function of acidity are represented vs. the  $H^+/H_2$  system (dashed lines) in Figures 6, 7, 9, and 10 (see section V) in dotted lines taking into account carbonium ions and in full lines without carbonium ions formation.

The position of the redox couple  $R^+/RH$  vs. the  $H^+/H_2$  system leads to the calculation of the oxidation pH,  $pH_R$ , or acidity level ( $H_R$  or  $R_0(H)_R$ ) for which the oxidation reaction 6 becomes quantitative (Figure 4):



$$pH_R = \frac{2F}{2.3RT} (E^\circ(H^+/H_2) - E^\circ(R^+/RH))$$

TABLE VIII. Acidity Levels of Oxidation of Alkanes into Carbenium Ions,  $pH_R$  in HF,  $H_R$  or  $R_0(H)_R$

alkane	$pH_R$	$H_R$	$R_0(H)_R$
$C_1H$	34	56	62
$C_2H$	17	40	46
$C_3H$	4.3	26.4	32.2
$n-C_4H$	5.6	27.7	33.5
$i-C_4H$	2.0	20.1	25.9
$n-C_5H$	5.2	27.3	33.1
$i-C_5H$	2.7 <sup>b</sup>	19.4	25.2
neo- $C_5H$	21	43	49
$n-C_6H$	5.0	27.1	32.9
2MPH	3.0	19.1	24.9
3MPH	2.4	19.7	25.5
22DMBH	1.5	23.6	29.4
23DMBH	3.5	18.6	24.4

<sup>a</sup> Reaction 6 becomes quantitative when the acidity level is higher than the one of point R ( $H < H_R$ ). <sup>b</sup> Experimental value from ref 23.

TABLE IX. Acidity Levels of Disproportionation of the Radical Oxidation State  $RR(R^{\cdot})$ ,  $pH_D$  in HF,  $H_D$  or  $R_0(H)_D$

alkane	$pH_D$	$H_D$	$R_0(H)_D$
$C_1H$	28	50	56
$C_2H$	15	37	43
$C_3H$	2.8	24.9	29.7
$n-C_4H$	3.6	25.7	31.5
$i-C_4H$	5.7	16.4	22.2
$n-C_5H$	2.4	24.5	30.3
$i-C_5H$	5.7 <sup>b</sup>	16.4	22.2
neo- $C_5H$	17	39	45
$n-C_6H$	1.9	20.2	26.0
2MPH	7.5	14.6	20.4
3MPH	7.8	14.3	20.1
22DMBH	8.7	13.4	19.2
23DMBH	10.5	11.6	17.4

<sup>a</sup> Reaction 14 becomes quantitative when the acidity level is lower than the value of point D ( $H > H_D$ ). <sup>b</sup> Experimental value from ref 23.

The values of  $pH_R$  in HF,  $H_R$ , and  $R_0(H)_R$  are reported in Table VIII. The alkanes methane, ethane, and neopentane, which are oxidized into primary carbenium ions, present very highly negative values of  $pH_R$ . This means that the oxidizing power of  $H^+$  ion is not high enough to oxidize these alkanes into  $R^+$  in the acidity range of superacid media.

The potential-acidity diagrams show the existence domain of the radical oxidation state, characterized by the dimer  $R-R$ . The area of this domain are reduced when the stability of the corresponding carbenium ion increases. The upper limit ( $pH_D$ , acidity level of disproportionation of the radical oxidation state) is calculated according to

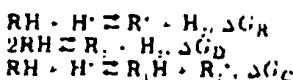
$$pH_D = \frac{F}{2.3RT} (E^\circ(RR/RH) - E^\circ(R^+/RR))$$

The values of  $pH_D$  in HF,  $H_D$  and  $R_0(H)_D$  are reported in Table IX. The negative values of  $pH_D$  mean that the radical oxidation state exists in the whole acidity range of HF; furthermore, according to the position of the  $H^+/H_2$  system, the oxidation of RH by  $H^+$  is endoenergetic and leads to the radical state RR; the carbenium oxidation state cannot be reached with  $H^+$  as the oxidizing agent.

We have to point out that (i) the isomerization of carbenium ion into a more stable ion displaces the  $pH_D$  value of the parent alkane toward 1 over acidic media— $pH_D$  increases but is still lower than the  $pH_D$

## Thermodynamic Behavior of Alkanes

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TABLE X. Gibbs Free Energies In Hydrogen Fluoride of the Basic Reactions of Alkanes (kcal mol<sup>-1</sup>)

alkane	$\Delta G_R$	$\Delta G_D$	$\Delta G_C$
C <sub>2</sub> H	43	8	
C <sub>3</sub> H	22	3.3	35
C <sub>4</sub> H	5.4	1.8	16
n-C <sub>5</sub> H	7.0	2.3	18
t-C <sub>5</sub> H	-2.5	4.6	0.9
n-C <sub>6</sub> H	6.5	3.3	18
i-C <sub>6</sub> H	-3.4	3.7	2.5
neo-C <sub>6</sub> H	26	5.1	7.0
n-C <sub>7</sub> H	6.2	8.3	18
2MPH	3.8	5.5	2.3
3MPH	-3.0	6.5	1.4
22DMBH	1.9	12.2	7.8
23DMBH	4.4	8.3	4.7

value of the isomerized alkane;<sup>26</sup> (ii) the values of pH<sub>D</sub> increase when the carbon atoms number of the alkane skeleton is increased, traducing the stability increase of the corresponding carbenium ions; (iii) the pH<sub>D</sub> values are displaced toward lower acidity levels when the temperature decreases.<sup>113</sup>

IV. Thermodynamics of Oxidation of Alkanes by H<sup>+</sup>

The potential-acidity diagrams of alkanes are restricted to the redox couples that are related to the reactivity of a C-H bond. In fact, the reactions of alkanes in superacid media lead to the formation of compounds with a lighter molecular weight than the initial alkanes. These cracking reactions, which are similar to the disproportionation reaction 14, are related to the reactivity of C-C bonds. This reactivity cannot be easily represented in the potential-acidity diagrams, but it is related to the thermochemical potential of the redox couples of alkanes. Therefore, these reactions can be estimated for any alkane in the considered set.

## A. Oxidation of C-H Bonds

The potential-acidity diagrams of alkanes show two types of oxidation of the C-H bond according to the acidity level of the medium: oxidation of alkanes into carbenium ion; oxidation of alkanes into radical that gives at first dimer and then oligomers.

## 1. Oxidation Into Carbenium Ion

The Gibbs free energy  $\Delta G_R$  of reaction 6 is related



to the standard potentials of the redox couples H<sup>+</sup>/H<sub>D</sub> and R<sup>+</sup>/RH, according to the relation

$$\Delta G_R = -2F(E^\circ(\text{H}^+/\text{H}_D) - E^\circ(\text{R}^+/\text{RH}))$$

The  $\Delta G_R$  values for the various alkanes are reported in Table X. As is expected according to the potential-acidity diagrams, the  $\Delta G_R$  values decrease when the molecular weight of the alkane is increased. Tertiary alkanes present quite exoenergetic oxidation processes.

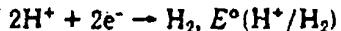
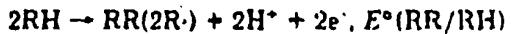
## 2. Oxidation Into the Radical Oxidation State

When the acidity level of the medium in which RH is dissolved is too low (H > H<sub>D</sub> or R<sub>0</sub>(H) > R<sub>0</sub>(H)<sub>D</sub>), the

oxidation of RH by H<sup>+</sup> does not give the carbenium ion but stops at the radical oxidation state. The products are at first dimers and then oligomers. The initial oxidation reaction is expressed as follows:



This oxidation reaction is the sum of the electrochemical reactions



The Gibbs free energy  $\Delta G_D$  of the condensation reaction 21 is related to the standard potentials of the redox couples RR/RH and H<sup>+</sup>/H<sub>D</sub> according to

$$\Delta G_D = -2F(E^\circ(\text{H}^+/\text{H}_D) - E^\circ(\text{RR}/\text{RH}))$$

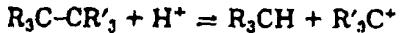
The  $\Delta G_D$  values for the different alkanes are reported in Table X. They are positive for any hydrocarbon, which means that the radical dimerization is always endoenergetic.

## B. Oxidation of C-C Bonds

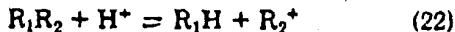
In the processes of isomerization or alkylation of alkanes, a more or less important ratio of the hydrocarbon load is converted by cracking in low molecular-weight products. The formation of such compounds has been explained by two principal reactions: the protolysis of alkanes by H<sup>+</sup> ion,<sup>104,150,169,170</sup> and the β scission of a carbenium ion.<sup>166,167,171</sup>

## 1. Protolysis of Alkanes

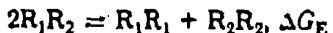
The protolysis is a C-C bond oxidation by H<sup>+</sup> ion that is similar to the reverse reaction of the alkylation (eq 14). The protolysis is represented as



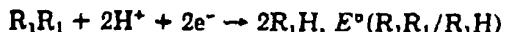
that is, by the scheme



Thermodynamically, this reaction is expressed by the sum of the chemical and electrochemical reactions



and



The Gibbs free energy  $\Delta G_C$  of the protolysis of R<sub>1</sub>R<sub>2</sub> is calculated according to

$$\Delta G_C = 1/2\Delta G_E - F(E^\circ(\text{R}_1\text{R}_1/\text{R}_1\text{H}) - E^\circ(\text{R}_2^+/\text{R}_2\text{R}_2))$$

Thus, taking into account this relation, the thermodynamic products of alkanes protolysis are determined. They are reported in Table XI with the corresponding values of  $\Delta G_C$  ( $\Delta G$ 's are also reported in Table X).

Furthermore, the acidity levels of protolysis (pH<sub>C</sub> in HF, H<sub>C</sub>, and R<sub>0</sub>(H)<sub>C</sub>) are calculated by using the same procedure as for oxidation acidity levels (pH<sub>R</sub> in HF, H<sub>R</sub>, and R<sub>0</sub>(H)<sub>R</sub>; see section IIIE). The pH<sub>C</sub> value is calculated by

$$2.3RT \text{pH}_C = -\Delta G_C$$

The values of pH<sub>C</sub>, H<sub>C</sub>, and R<sub>0</sub>(H)<sub>C</sub> are reported in Table XII. The values represent the acidity levels that

TABLE XI. Protolysis of Alkanes in Hydrogen Fluoride<sup>a</sup>  
 $R_1R_2 + H^+ \rightleftharpoons R_1H + R_2^+$  (22)

alkane, $R_1R_2$	$\Delta G_C$	$R_1H, R_2^+$	$\Delta G_C$	$R_1H, R_2^+$
$C_2H$	35	$C_2H, C_2^+$		
$C_3H$	16	$C_3H, C_2^+$		
$n-C_4H$	18	$C_4H, C_3^+$		
$i-C_4H$	0.9	$C_4H, C_3^+$		
$n-C_5H$	18	$C_5H, C_4^+$		
$i-C_5H$	2.5	$C_5H, n-C_4^+$	3.4	$C_5H, C_4^+$
$neo-C_5H$	7.0	$C_5H, i-C_4^+$		
$n-C_6H$	18	$n-C_6H, C_5^+$		
2MPH	2.3	$C_6H, n-C_5^+$	3.3	$C_6H, C_5^+$
3MPH	1.4	$C_6H, n-C_5^+$	4.3	$C_6H, n-C_5^+$
22DMBH	7.8	$C_6H, i-C_5^+$	6.9	$C_6H, i-C_5^+$
23DMBH	4.7	$C_6H, i-C_5^+$	2.4	$C_6H, C_5^+$

<sup>a</sup> Gibbs free energy of the protolysis (kcal mol<sup>-1</sup>) and nature of the cracking products.

TABLE XII. Acidity Levels of Protolysis of Alkanes,  $pH_C$  in HF,  $H_C$ , and  $R_0(H)_C$ <sup>a</sup>  
 $R_1R_2 + H^+ \rightleftharpoons R_1H + R_2^+$  (22)

alkane	$pH_C$	$H_C$	$R_0(H)_C$
$C_2H$	~ -28	~ -50	~ -56
$C_3H$	~ -13	~ -35	~ -41
$n-C_4H$	~ -14	~ -36	~ -42
$i-C_4H$	~ -0.7	~ -22.8	~ -28.6
$n-C_5H$	~ -14	~ -36	~ -42
$i-C_5H$	~ -2.0	~ -24.1	~ -29.9
$neo-C_5H$	5.6	~ -16.5	~ -22.3
$n-C_6H$	~ -14	~ -36	~ -42
2MPH	~ -1.8	~ -23.9	~ -29.7
3MPH	~ -1.1	~ -23.2	~ -29.0
22DMBH	6.2	~ -15.9	~ -21.7
23DMBH	3.8	~ -18.3	~ -24.1

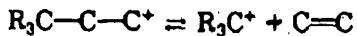
<sup>a</sup> Reaction 22 becomes quantitative when  $H < H_C$  ( $pH_C < pH_C$  or  $R_0(H) < R_0(H)_C$ ).

must be reached in order to render the protolysis quantitative: when  $H < H_C$  protolysis 22 is displaced toward the right.

Linear alkanes or light alkanes present highly positive  $\Delta G_C$  values (Tables X, XI); thus, they will not be cracked by protolysis in superacid media. The oxidation of a C-C bond is enhanced when the size or the branching of the alkane is increased. This reaction can be quite exoenergetic; see, for example, neopentane or neohexane (22DMBH). The reactivity of these latter alkanes is characterized by protolysis (see section V).

## 2. $\beta$ Scission of Carbenium Ions

The  $\beta$  scission of a carbenium ion is the breaking of the C-C bond, which is in  $\beta$  position vs. the positive charge, with formation of a new carbenium ion and an alkene:



This reaction is represented as follows:



The Gibbs free energy  $\Delta G_\beta$  of this reaction is calculated by the relation

$$\Delta G_\beta = \Delta G_f(R_1^+) + G_f(R_2^+) - \Delta G_f(R_1R_2^+)$$

Through these calculations, the thermodynamic products of this reaction are determined; they are reported in Table XIII, with the corresponding values of

TABLE XIII.  $\beta$ -Scission Reaction of Alkycarbenium Ions in Hydrogen Fluoride<sup>a</sup>

alkane, $R_1R_2$	$\Delta G_C$	$R_1H, R_2^+$	$\Delta G_C$	$R_1H, R_2^+$
$C_2^+$	43	$C_2^+, C_2^+$	47	$C_2^+, C_2^+$
$nC_3^+$	44	$C_3^+, C_3^+$	30	$C_3^+, C_3^+$
$iC_4^+$	54	$C_4^+, C_4^+$	40	$C_4^+, C_4^+$
$nC_5^+$	28	$C_5^+, C_5^+$	14	$C_5^+, C_5^+$
$iC_6^+$	33	$C_6^+, C_6^+$	32	$C_6^+, C_6^+$
$neoC_6^+$	24	$C_6^+, iC_5^+$	5	$C_6^+, iC_5^+$
$nC_7^+$	33	$C_7^+, n-C_6^+$	23	$C_7^+, n-C_6^+$
2MP $^+$	23	$C_7^+, C_7^+$	10	$C_7^+, C_7^+$
3MP $^+$	33	$C_7^+, n-C_6^+$	23	$C_7^+, n-C_6^+$
22DMB $^+$	19	$iC_6^+, C_6^+$	18	$iC_6^+, C_6^+$
23DMB $^+$	29	$C_6^+, C_6^+$	15	$C_6^+, C_6^+$

<sup>a</sup> Gibbs free energies of reactions (kcal mol<sup>-1</sup>) and nature of the products.

In superacid media, it has been shown that most alkenes are protonated into carbenium ions (see Table VI, section IIIC). Hence, the  $\beta$ -scission reaction has to be represented as follows:



The Gibbs free energy of this reaction is then expressed by

$$\Delta G_\beta' =$$

$$\Delta G_f(R_1^+) + \Delta G_f(R_2^+) - \Delta G_f(R_1R_2^+) - \Delta G_f(H^+)$$

which is also related to the above calculated  $\Delta G_\beta$  according to the relation

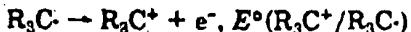
$$\begin{aligned} \Delta G_\beta' &= \Delta G_\beta + 2.3RT(-22.1 - H_p(R_{2n})) \\ &= \Delta G_\beta + 2.3RT(-27.9 - R_0(H)p(R_{2n})) \end{aligned}$$

where -22.1 (or -27.9) is the acidity level  $H$  (or  $R_0(H)$ ) of hydrogen fluoride ( $[H^+] = 1$  M, standard reference) and  $H_p(R_{2n})$  (or  $R_0(H)p(R_{2n})$  protonation).

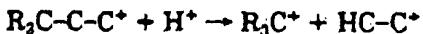
The different calculations of  $\Delta G_\beta'$  lead to the determination of the thermodynamic products, which are reported in Table XIII with the corresponding  $\Delta G_\beta'$  values.

According to the  $\Delta G$  values of protolysis (Table XI) and  $\beta$  scission (Table XIII), the protolysis reaction is more exoenergetic than the  $\beta$ -scission one. This result may be traduced in terms of oxidation state: The protolysis, which is similar to the disproportionation of the radical oxidation state, is an oxidation of  $R_2^+$  into  $R_2^+$  and a reduction of  $R_1^+$  into  $R_1H$ .

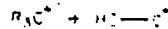
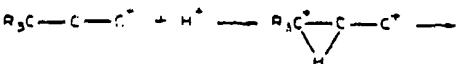
The  $\beta$ -scission (reaction 24) may be represented by the electrochemical reactions



whose sum is, of course, the  $\beta$ -scission reaction:



Therefore, this reaction may be regarded as a disproportionation, but at a higher oxidation state than the protolysis, that is, an oxidation by  $H^+$  of the C-C bond in  $\beta$  vs. the positive charge:



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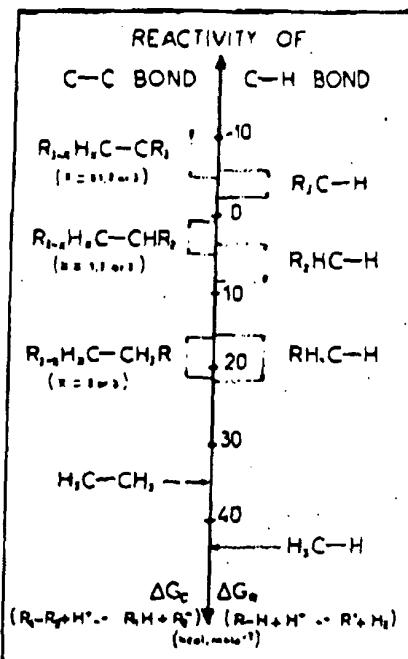
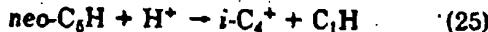


Figure 5. Thermodynamic reactivity scale of C-C and C-H bonds as a function of the alkane structure.

This high oxidation intermediate explains the fact that the cracking of carbenium ions is only observed in superacid media for cations having at least five carbon atoms.<sup>15,16,104,170</sup> The principal product is the  $i\text{-}C_4^+$  cation, which is very stable at this acidity level.

In contrast, when alkanes are dissolved in superacid media, the cracking goes through a protolysis of the C-C bond<sup>24,103,104,170,172-174</sup> that can be quite exoenergetic (Table XI). The best example is the protolysis of neopentane in superacid media ( $H < -19$ ) according to



In superacid solutions of carbenium ions with reducing agents such as  $H_2$  or RH, the cracking of these cations may go through a reduction into alkane, followed by a protolysis. These two steps prevent to go through the high oxidation state (radical cation  $C-C^+$ ) involved in the  $\beta$ -scission reaction. In this way, the cracking of the methylcyclopentane ring has been shown to proceed via a protolysis of MCPH and not through the  $\beta$  scission of  $MCP^+$ <sup>24</sup> as was suggested.<sup>173,178</sup>

When no reducing agents are present, the cracking of carbenium ions has to proceed via the  $\beta$  scission.  $H^+$  is then the oxidant, and, with respect to its oxidizing power, such a cracking is weak. Its importance increases with the size of the cations or by raising the temperature.<sup>15,16</sup>

### C. Reactivity Scale of C-H and C-C Bonds

According to the calculated values of  $\Delta G_R$ , the Gibbs free energy of C-H bond oxidation, a thermodynamic scale of the C-H bond reactivity as a function of the substituents is represented in Figure 5. When the same procedure is used and the calculated values of  $\Delta G_C$ , protolysis of a C-C bond, are considered, a thermodynamic scale of the C-C bond is placed against one of the C-H bond in Figure 5.

As expected, the reactivities of C-C and C-H bonds are the highest when their oxidations lead to the for-

mation of tertiary carbenium ions that are very stable in superacid media. The reactivity for an alkane is related to the electron density in the skeleton that causes basic sites. These "negative" places constitute the targets of the electrophilic reactions in superacid media. The scale presented in Figure 5 is in good agreement with the experimental reactivity order, reported by Olah et al.<sup>102,103</sup>

The conclusions must be moderated by the kinetic parameters and steric hindrance that can modify the occurrence of any reaction, that is, the thermodynamic reactivity order.

### V. Chemical Behavior of Alkanes

Despite the uncertainties on the establishment of the thermochemical properties of alkanes, an examination of the potential-acidity diagrams leads to interesting conclusions concerning the behavior of alkanes in superacid media that depends on their nature and the acidity level of the medium.

The potential-acidity diagram shows, as a function of the acidity level, the alkane oxidation state that is reached by oxidation. This oxidation state is determined by the oxidizing power of the involved redox couple that we limited to the  $H^+/H_2$  system. It stands to reason that a higher oxidation state can be reached when oxidants higher than  $H^+$  are involved, such as  $SO_3$  in  $HSO_3F$ ,<sup>91</sup> alkylcarbenium ion,<sup>177-178</sup> or fluoranil<sup>163</sup> in HF.

The established diagrams are restricted to the initial reactions of alkanes. Thus, the condensation products, for example, being much more reactive than the starting compounds, react according to their diagrams and complicate the overall process. Therefore, kinetic data are needed for the description of the reactions, and they are briefly summarized.

#### A. Typical Kinetic Parameters of the Basic Processes

The mechanism of acid-catalyzed hydrocarbon conversions has been the subject of numerous studies. It is generally agreed that the overall processes comprise two basic reactions, namely, (1) a redox reaction, oxidation of C-H or C-C bonds to yield carbenium ions or the reverse, and (2) skeleton rearrangements of the carbenium ions.

Much work has been devoted to the measurements of the rate constants of the various reactions: NMR spectroscopy has been shown to be suitable for the study of skeleton rearrangements,<sup>14-16,161,162</sup> rate constants of the redox reactions have been determined in HF-SbF<sub>5</sub>,<sup>25,103,105,106,167,169</sup> and related media,<sup>25,171</sup>  $R_3SO_3H$  media (neat or SbF<sub>5</sub> mixtures),<sup>183,184</sup>  $HSO_3F$ ,<sup>57,185</sup> or less acidic media.<sup>57,174</sup> Typical values of rate constants for the different basic reactions in highly superacid media ( $H < -20$ ) are reported in Table XIV. They vary, of course, with the particular skeleton structures of the species involved. As expected, the rate constants of  $H^+$  oxidation increase when the acidity level is raised.<sup>25,57,183,184</sup> Furthermore, when a different oxidant is involved, such as  $SO_3$  in  $HSO_3F$ , the oxidation rate constant of alkanes is quite increased.<sup>163</sup>

The mechanisms of rearrangement of the carbenium ions were paid considerable attention in the literature,

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Fabre, Devynck, and Tremillon

TABLE XIV. Kinetic Parameters of Reactions of Alkane in Superacid Media ( $H < -20^\circ$ )<sup>a</sup>

redox reaction <sup>a</sup>	rate constant k at 0 °C
$R^+ + RH \rightarrow R^{\cdot} + H_2$	$10^{-1}-10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$
$H_2 + R^{\cdot} \rightarrow RH + H^{\cdot}$	$10^{-1}-10^{-3} \text{ atm}^{-1} \text{ g}^{-1}$
$R^{\cdot}R^{\cdot} \rightarrow H^{\cdot} + R, H^{\cdot} + R^{\cdot}$	$10^{-1}-10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$
$t-R, H^{\cdot} \rightarrow i-R, ^{\cdot} + t-R, H^{\cdot}$	$\sim 10 \text{ L mol}^{-1} \text{ s}^{-1}$
$sec-R, H^{\cdot} \rightarrow t-R, ^{\cdot} + sec-R, H^{\cdot}$	$10^{-1} \text{ L mol}^{-1} \text{ s}^{-1}$
rearrangement reaction <sup>b</sup>	rate constant at 0 °C
$R^{\cdot} \rightarrow R^{\cdot}$	$> 10^3 \text{ s}^{-1}$ at -80 °C
(X = H or CH <sub>3</sub> )	
$R^{\cdot} \rightarrow R^{\cdot}$	$10^{-1}$
$R^{\cdot} \rightarrow R^{\cdot}$	$10^{-1}-2 \text{ s}^{-1}$
$R^{\cdot} \rightarrow R^{\cdot}$	$6 \times 10^{-2} \text{ s}^{-1}$

<sup>a</sup> See section VA. <sup>b</sup> Reference 122.

in particular the question of knowing whether primary ions can occur as intermediates and whether cyclic intermediates such as protonated cyclopropanes are involved.<sup>121,122,184-185</sup> The formation of protonated cyclopropanes would explain the fact that in HF-SbF<sub>5</sub>, *n*-butane is not isomerized because the pathway implies going through a primary ion.<sup>121</sup> In less acidic media, the isomerization of primary ions such as neopentyl cation has been explained by a bimolecular process.<sup>187-189</sup>

Whatever the mechanisms of skeleton rearrangements are, Table XIV shows that they are faster than the redox reactions that are the rate-determining steps of the overall processes. In the acid-catalyzed alkane isomerization, represented as follows:



The process is rate determined by reaction 1 during the induction time, which corresponds to the acid phase formation.<sup>120,188,187,181</sup> Once the acid phase is saturated with *n*-R<sup>·</sup> and *i*-R<sup>·</sup> cations, reaction 3 completes the isomerization cycle and rate determines the process. Thus, the conditions of carbenium ion formation are of prime importance in the isomerization process of alkanes.

## B. Isomerization of Alkanes

The alkanes considered in this reaction are the hydrocarbons from butanes up to hexanes. Their principal reactivity concerns the isomerization of normal alkanes into tertiary alkanes, which is of great interest for upgrading of motor fuels. Numerous processes have been reported in highly superacid media: HF, HSO<sub>3</sub>F, or R<sub>2</sub>SO<sub>3</sub>H/SbF<sub>5</sub> or TaF<sub>5</sub> mixtures,<sup>184-200</sup> which means that  $H < -18$ .

According to the general schematic representation of the isomerization process (reactions 1-3), the carbenium ion formation has to be enhanced. Then, when the potential-acidity diagrams of these alkanes are considered, the direct oxidation of RH into R<sup>·</sup> only takes

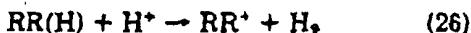
place in media of acidity levels higher than the one of the radical oxidation state dismutation, point D in the diagrams, which means that  $H < H_D$  or  $R_0(H) < R_0(H)_D$  (see Table IX).

The values of  $H_D$  or  $R_0(H)_D$  reported in Table IX for *n*-alkanes are calculated without taking into account the isomerization of the *n*-R<sup>·</sup> ion. This reaction displaces  $H_D$  or  $R_0(H)_D$  toward positive values;<sup>25</sup> the upper limit is the  $H_D$  or  $R_0(H)_D$  values of the corresponding tertiary alkanes.

Furthermore, the direct oxidation of RH into R<sup>·</sup> becomes quantitative when the acidity level of the medium is higher than the oxidation one, point R in the diagrams, which means  $H < H_R$  or  $R_0(H) < R_0(H)_R$  (see Table VIII).

In contrast, when the acidity level of the medium is too low ( $H > H_D$  or  $R_0(H) > R_0(H)_D$ ), the H<sup>+</sup> oxidation of RH does not lead to the carbenium ion but stops at the radical oxidation state, yielding at first the dimer RR. This oxidation is slightly endoenergetic ( $\Delta G_D$ ; see Table X), and the process is complex, yielding condensation and cracking products. In this way, a radical initiation of *n*-alkane isomerization in low acidic media has been reported. The isomerization of *n*-pentane<sup>201</sup> and *n*-butane<sup>202</sup> is carried out in neat perfluoroalkane-sulfonic acids, whose acidity levels ( $H \sim -14$ ) are, of course, higher than the  $H_D$  values of these alkanes (Table IX).

The dimer, being much more reactive than the initial compound, is oxidized into the carbenium ion RR<sup>·</sup> as follows:

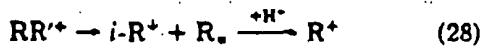


which is isomerized into different cations

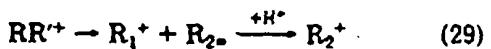


From that point, two pathways leading to the same products may be suggested,<sup>201,202</sup> namely (1)  $\beta$  scission of the carbenium ion and (2) protolysis of RR'(H) resulting from the reduction of RR<sup>·</sup>.

(1) The  $\beta$  scission of RR<sup>·</sup> yields the  $\alpha$ -carbenium ion *i*-R<sup>·</sup> and an alkene or cracking products, as follows:



or



These new carbenium ions are then reduced to yield the corresponding alkanes.

(2) The protolysis route implies an initial reducing step that can be quite fast (Table XIV); for example:



The next step is the protolysis of the alkane into the isoalkane *i*-RH and a carbenium ion or cracking products, as follows:



or



From the thermodynamic point of view (section IV), the protolysis reactions are more exoenergetic than the

## Thermodynamic Behavior of Alkanes

$\beta$ -scission reactions. Thus, it is highly probable that isomerization in low acidic media ( $H > H_D$ ) proceeds through dimerization and protolysis. Anyhow, such isomerizations give bad yields and wide product distribution (cracked, isomerized, and condensation products).

Taking into account the two basic processes, the chemical behavior of these alkanes can be reviewed.

## 1. Butanes (Figure 6)

The behavior of *n*-butane is one of the most striking and controversial. In highly superacid media, HF or  $\text{HFO}_3\text{F}/\text{SbF}_5$ ,  $H < -18$ , *n*-butane was claimed to be isomerized<sup>104,170,192</sup> into isobutane, while other works gave evidence of the oxidation process only.<sup>121,203,204</sup> In fact, if the carbenium ion rearrangements are assumed to proceed through protonated cyclopropanes, *n*-butyl ion cannot be isomerized into *tert*-butyl ion and leads only to carbon scrambling in the skeleton.<sup>121</sup> These different behaviors may be explained by taking into account the acidity level of the medium: the oxidation of *n*-butane into *n*-butyl ion takes place in the highest superacid media, HF-SbF<sub>5</sub>,<sup>121</sup> which means that  $H < H_D$  (*n*-C<sub>4</sub>H); the isomerization of *n*-butane is observed in less acidic media, such as  $\text{HSO}_3\text{F}-\text{SbF}_5$ ,<sup>104,170</sup> or R<sub>F</sub>SO<sub>3</sub>H.<sup>202</sup> In these latter media, the process is initiated by radicals and goes through dimers.<sup>202</sup> Then, the acidity level is lower than the radical dismutation one:  $H > H_D$  (*n*-C<sub>4</sub>H), which is in good agreement with the calculated  $H_D$  values.

In contrast with the probable "radical" isomerization of *n*-butane, the *n*-butyl ion isomerization, where *n*-C<sub>4</sub><sup>+</sup> results from acid-base reactions of RX with H<sup>+</sup>,<sup>192</sup> may be explained by a bimolecular cationic reaction.

In contrast, the behavior of isobutane is quite clear. In superacid media,  $H < H_D$  (*i*-C<sub>4</sub>H), the oxidation of *i*-C<sub>4</sub>H into *i*-C<sub>4</sub><sup>+</sup> takes place and is nearly quantitative in the highest acid media, HF-SbF<sub>5</sub>.<sup>120,150</sup> The carbenium ion *i*-C<sub>4</sub><sup>+</sup> is one of the most stable cations.<sup>104,108,170</sup> In a solvent where  $H > H_D$  (*i*-C<sub>4</sub>H), isobutane is alkylated by carbenium ions for the synthesis of motor fuels (see section VD).

## 2. Pentanes (Figure 7)

The isomerization of *n*-pentane has been studied in various media: HF-SbF<sub>5</sub>,<sup>120,168,167</sup>  $\text{HSO}_3\text{F}-\text{SbF}_5$ ,<sup>104,170,206-207</sup>  $\text{HSO}_3\text{F}$ ,<sup>188</sup> and R<sub>F</sub>SO<sub>3</sub>H (neat or with SbF<sub>5</sub>).<sup>181,182,201,207</sup> According to the product distribution, the two basic processes are observed. Typical product distributions are represented in Figure 8 for two media: HF-SbF<sub>5</sub>,  $H \sim -22.7$ , and C<sub>2</sub>F<sub>5</sub>SO<sub>3</sub>H,  $H \sim -14$ .

In HF-SbF<sub>5</sub>, the oxidation of *n*-C<sub>5</sub>H directly gives the *n*-C<sub>5</sub><sup>+</sup> cation which is isomerized into *i*-C<sub>5</sub><sup>+</sup> ion. The overall process corresponds to the general scheme (reactions 1-3) and leads to a thermodynamic *n*-C<sub>5</sub>H conversion.<sup>168,167</sup> No condensation products result, but a few cracked products (up to 1%) are formed, probably through the protolysis of isopentane (see Table XI). Thus, the acidity level of HF-SbF<sub>5</sub> corresponds to  $H < H_D$  (C<sub>5</sub>H).

In C<sub>2</sub>F<sub>5</sub>SO<sub>3</sub>H, the *n*-C<sub>5</sub>H conversion is very slow, and large amounts of condensation products are recovered. The process goes through the radical oxidation state and can be radically initiated.<sup>201</sup> The initial formation of the dimer leads to complex reactions; a wide product

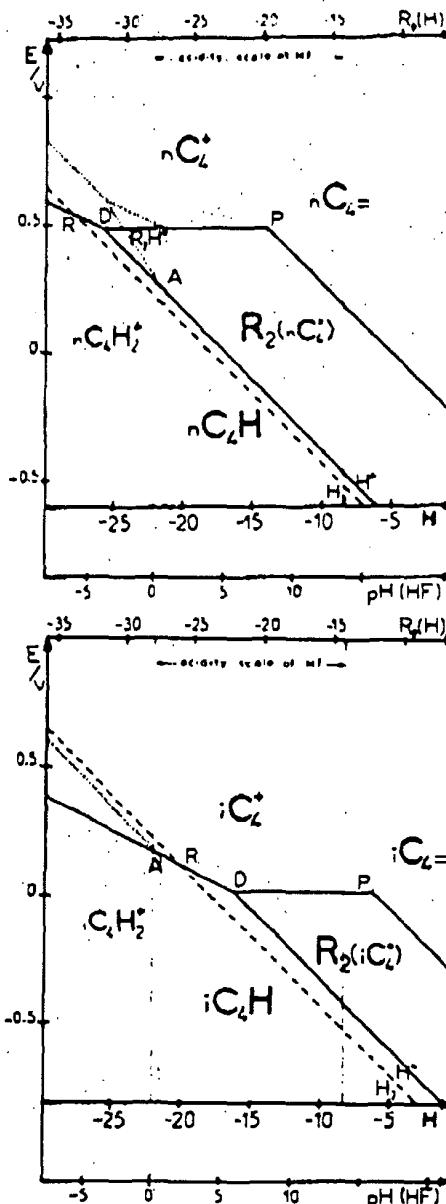
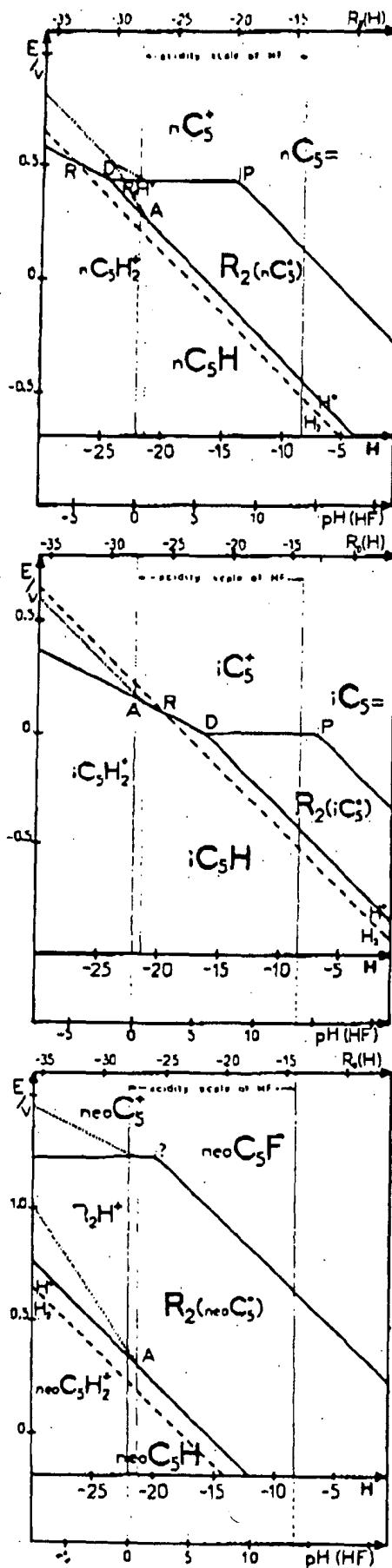


Figure 6. Potential-acidity diagrams of butanes (*n*-C<sub>4</sub>H and *i*-C<sub>4</sub>H) in superacid media. The diagrams are plotted vs. the H<sup>+</sup>/H<sub>2</sub> system (dashed line); dotted lines considering the protonation of the alkane and full lines without carbonium ion formation. The acidity scale in HF (pH(HF)) is plotted against the  $H$  and  $R_D(H)$  acidity functions (Figure 3, section II B).

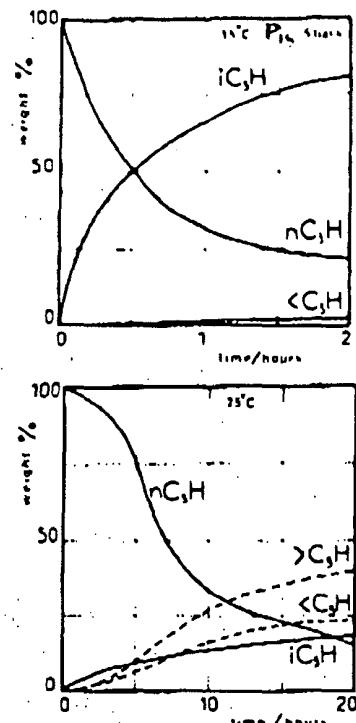
distribution is obtained and the conversion ratio is very low. The acidity level corresponds, of course, to  $H > H_D$  (C<sub>5</sub>H).

The two media mentioned above represent the utmost media in which the two basic processes are separately involved.  $\text{HSO}_3\text{F}-\text{SbF}_5$  mixtures yield products similar to those in HF-SbF<sub>5</sub>. The other solvents, whose acidity levels stand between the ones of the two media mentioned above, lead to the occurrence of the two processes. The conversion ratio is nearly thermodynamic, but a few condensation products, and consequently cracked compounds, are recovered.

As for isobutane, the oxidation of isopentane yields the corresponding carbenium ion *i*-C<sub>5</sub><sup>+</sup> in a wide acidity range.<sup>23</sup> The *i*-C<sub>5</sub><sup>+</sup> cation is very stable at room temperature; by increasing the temperature, above 100 °C, it is converted into the *tert*-butyl cation *t*-C<sub>4</sub><sup>+</sup>.<sup>104,170</sup>



**Figure 7.** Potential-acidity diagrams of pentane in superacid media: *n*-C<sub>5</sub>H<sub>12</sub>, *n*-pentane; *i*-C<sub>5</sub>H<sub>12</sub>, isopentane; neo-C<sub>5</sub>H<sub>12</sub>, neo-pentane; see Figure 6.

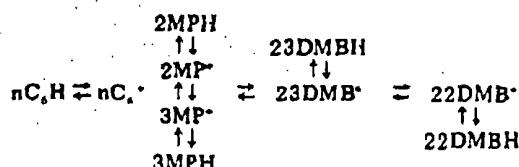


**Figure 8.** Isomerization of *n*-pentane ( $n\text{-C}_5\text{H}_{12}$ ) in superacid media: (A) in  $\text{HF-SbF}_3$  ( $H \sim -22.7$ ) (reprinted with permission of R. Bonifay<sup>120</sup>); (B) in  $\text{C}_2\text{F}_5\text{SO}_3\text{H}$  ( $H \sim -14$ ) (reprinted with permission of P. Ortega<sup>124</sup>).

The chemical behavior of neopentane is quite surprising. In very superacid media,  $\text{HF-SbF}_5$  or  $\text{HSO}_3\text{-F-SbF}_5$ , neopentane undergoes conversion into *tert*-amyl cation  $i\text{-C}_5^+$  at low temperature ( $T < -50^\circ\text{C}$ ),<sup>104,170</sup> and it is cracked by protolysis at room temperature<sup>102,104,160,169,170</sup> according to thermochemical calculations (section IVB, Tables X, XI). The dimer process may be suggested to explain the isomerization at low temperature. The  $\text{H}^+$  oxidizing power is too low to initiate the cationic isomerization through the primary  $\text{neo-C}_5^+$  ion (Figure 7). In contrast, when neopentyl ion  $\text{neo-C}_5^-$  is produced from neopentyl halide, the isomerization into  $i\text{-C}_5^+$  cation is observed but proceeds by a bimolecular reaction.<sup>189</sup>

### 3. Hexanes (Figure 9)

According to the potential-acidity diagrams of hexanes, their isomerization requires less acidic media than the ones needed for the isomerization of pentane. Hexanes are isomerized through the carbenium ion route in solvents such as HF-BF<sub>3</sub>,<sup>171</sup> or HF-TaF<sub>5</sub>.<sup>208</sup> In the highest superacid media (HF-SbF<sub>5</sub> or HSO<sub>3</sub>F-SbF<sub>5</sub>), the amount of cracking products becomes important.<sup>120,166,167,203,209</sup> The isomerization process of hexanes is represented as follows:<sup>170,171,203</sup>



The first products of *n*-hexane conversion are the monobranched alkanes 2MPH and 3MPH, whose carbonium ions are converted into the 23DMR<sup>+</sup>. This carbonium ion is the most stable cation of the hexyl

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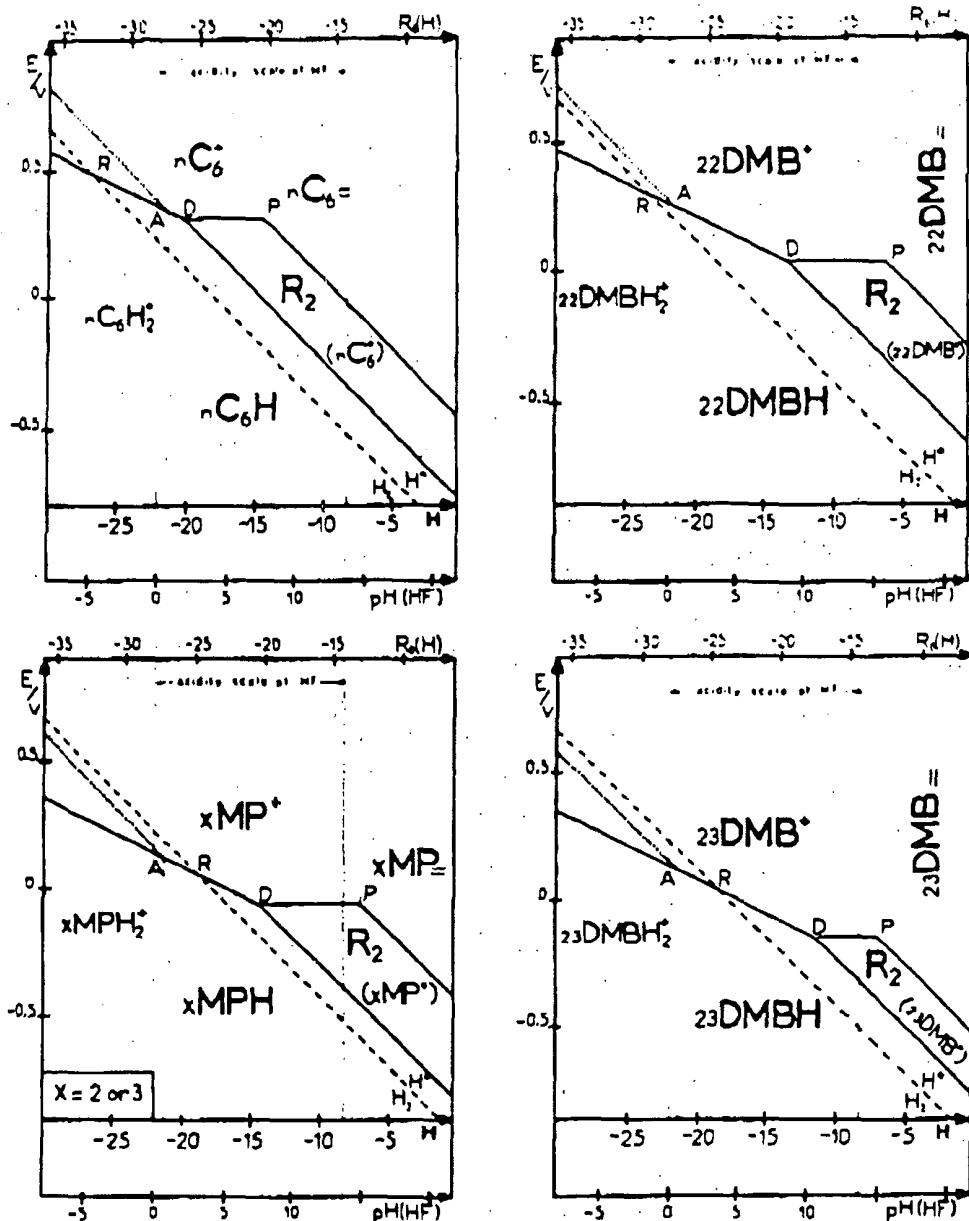
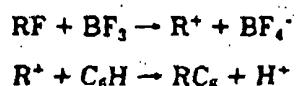


Figure 9. Potential-acidity diagrams of hexanes in superacid media:  $n\text{-C}_6\text{H}_6$ ,  $n\text{-hexane}$ ; 22DMBH, 2,2-dimethylbutane; 23DMBH, 2,3-dimethylbutane; 2MPH (2-methylpentane), 3MPH (3-methylpentane), presenting the same behavior, are represented by XMPH; see Figure 6.

ions<sup>14-16</sup> and yields, of course, the corresponding alkane 23DMBH by reduction. In a last step, the 23DMB<sup>+</sup> cation is isomerized into the 22DMB<sup>+</sup> cation, which is easily reduced into neohexane, 22DMBH.

This latter step, formation of the 22DMBH structure, would explain the occurrence of cracking products by protolysis of neohexane. Taking into account the  $\Delta G_C$  values of hexanes' protolysis (Tables X, XI), the protolysis of neohexane (22DMBH) is the most exoenergetic reaction and yields either isobutane and ethane or isopentane and methane. This is in good agreement with experimental results where the product distribution analysis shows that the amount of cracking products is related to the 22DMBH fraction.<sup>12,17</sup> The other tertiary hexanes may be cracked (Table XI); but, according to the oxidation equilibria  $K_R$ , their predominating forms are the carbenium ions, which are not easily cracked. In contrast, 22DMB<sup>+</sup> is easily reduced (Table X) into 22DMBH, which undergoes a protolysis.

In low acidic media, the isomerization of hexanes has been initiated by alkyl halide/BF<sub>3</sub>,<sup>17</sup> but the product distribution is wide: cracked, condensation, and isomerized compounds are recovered. This isomerization may proceed through a condensation process in which the oxidant is the alkylcarbenium ion, according to the reactions



The alkylated hexane leads to numerous products by oxidation, isomerization, and cracking.

Through the examples mentioned above, highly superacid solutions appear quite suitable for the isomerization of alkanes. In contrast, the lower acidic solutions ( $H > H_D$  of alkanes) present inconvenient properties: they induced wide product distribution resulting from the condensation route. In each case, a good agreement

between the calculated previsions and experimental results is observed. Thus, the examination of the diagrams presented for the selected alkanes leads to the choice of the appropriate medium for the isomerization.

The increase of the acidity level is a convenient way to enhance the isomerization of alkanes, but it also induces protolysis reactions yielding cracked products. According to the thermochemical calculations and through the examples presented, it is highly probable that the cracking is restricted to protolysis reactions in isomerization processes. The  $\beta$ -scission reaction, which involves an oxidation state higher than the carbenium ion state, would only take place in solvents where oxidants stronger than  $H^+$  are involved.

Thus, an equilibrium in the choice of the acidity level has to be found in order to enhance isomerization and to prevent cracking. Generally, high hydrogen pressures or addition of aromatic compounds are used to prevent the side reactions. In fact, both procedures decrease the  $H^+/H_2$  redox potential, according to the Nernst law and the basic nature of aromatic compounds. Then, the amount of cracked products is decreased, but isomerization is also inhibited.<sup>166,167,171</sup> According to the protolysis reactions that yield light alkanes, a simplest way to inhibit these reactions may be the use of methane or ethane, under high pressure, which acts on the protolysis only because of their very weak reactivities.

### C. Light Alkanes (Figure 10)

Alkanes from methane to propane present weak reactivities; the  $\Delta G$  values of any reaction are positive in any medium (Table X). According to their potential-acidity diagrams, the oxidizing power of  $H^+$  is too low to yield the corresponding carbenium ions.

In  $HSO_3F-SbF_5$  (1:1), oxidation of propane yields *tert*-butyl ion  $i-C_4^+$  and *tert*-hexyl ions.<sup>104</sup> This may be interpreted by dimer formation:

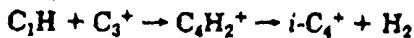


followed by the isomerization of hexanes and the protolysis of 22DMBH, which yields  $i-C_4^+$ .

The two lightest alkanes, methane and ethane, show practically no reactivity at low or room temperature. In  $HF-SbF_5$  or  $HSO_3F-SbF_5$  mixtures, hydrogen-deuterium exchanges have been observed at room temperature, according to the acid-base reaction.<sup>169,173,210</sup>



In  $HSO_3F-SbF_5$  (1:1), the oligocondensation of methane and ethane is observed by increasing the temperature and the alkane pressure.<sup>104,170,172,173</sup> Methane yields the *tert*-butyl cation while ethane yields  $i-C_4^+$  (90%) and 23DMB<sup>+</sup> (10%). To explain these reactions a cationic pathway was suggested, as follows:



The oligocondensation of methane stops at the very stable  $i-C_4^+$  carbenium ion.

When the  $H_D$  values (Table IX) and the potential-acidity diagrams of methane and ethane (Figure 10) are

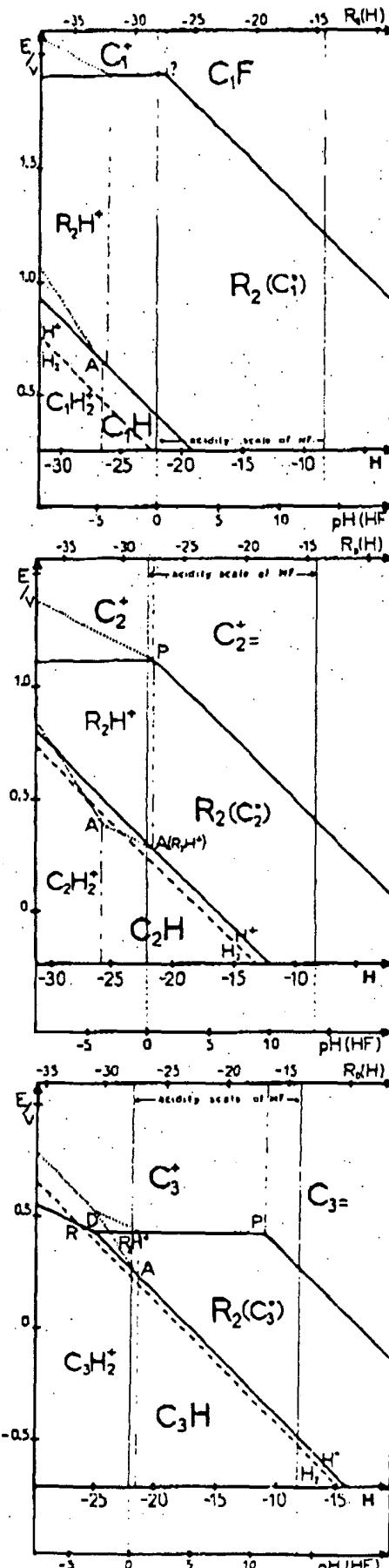


Figure 10. Potential-acidity diagrams of light alkanes in superacid media:  $C_1H$ , methane;  $C_2H$ , ethane;  $C_3H$ , propane; see Figure 6.

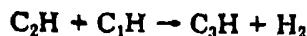
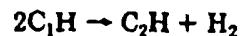
## Thermodynamic Behavior of Alkanes

TABLE XV. Gibbs Free Energies of the Basic Reactions between Methyl Ion and Alkanes in Hydrogen Fluoride (kcal m<sup>-1</sup>)

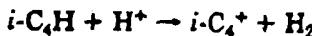


alkane, R'H	$\Delta G$	nature of the reaction	$\Delta G$	nature of the reaction
C <sub>1</sub> H	-33	alkylation		
C <sub>2</sub> H	-35	alkylation	-21	redox
C <sub>3</sub> H	-37	alkylation	-37	redox
n-C <sub>4</sub> H	-37	redox	-36	alkylation
i-C <sub>4</sub> H	-45	redox	-37	alkylation
n-C <sub>5</sub> H	-37	alkylation	-36	redox
i-C <sub>5</sub> H	-46	redox	-37	alkylation
neo-C <sub>5</sub> H	-42	cracking	-36	alkylation
n-C <sub>6</sub> H	-38	alkylation	-36	redox
2MPH	-46	redox	-35	alkylation
3MPH	-46	redox	-36	alkylation
22DMBH	-42	cracking	-41	redox
23DMBH	-47	redox	-40	cracking

taken into account, the H<sup>+</sup> activity is not high enough to yield the corresponding carbenium ions. The redox potential of the oxidant has to be very high in order to get the methyl ion from E° > 1.2 V, Table V. In this way, ozone is not a sufficient oxidant because its reaction with methane leads to C<sub>3</sub> or C<sub>4</sub> alkoxycarbenium ions,<sup>211</sup> whose formation may be interpreted by first steps of condensation. The resulting C<sub>3</sub> or C<sub>4</sub> alkane is then oxyfunctionalized. Therefore, the oligocondensation may go through the dimerization pathway involving the radical oxidation state, according to the reactions



At these acidity levels, isobutane is oxidized into i-C<sub>4</sub><sup>+</sup> ion:



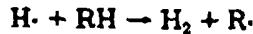
The oligocondensation of ethane yields the C<sub>6</sub><sup>+</sup> cations by trimerization and oxidation of the resulting C<sub>6</sub>H, and the i-C<sub>4</sub><sup>+</sup> cation by cracking of 22DMBH or dimerization and oxidation of the resulting butane.

According to the thermochemical properties of radicals,<sup>212-215</sup> whose heats of formation are lower than those of carbenium ions, it may be suggested that the oligocondensation proceeds through a radical process, as follows:

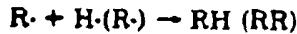
initiation by H<sup>+</sup> oxidation



propagation

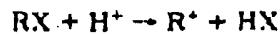


chain breaking

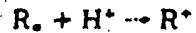


Such radical pathways may be suggested for the isomerization of n-butane and n-pentane in neat C<sub>2</sub>F<sub>5</sub>SO<sub>3</sub>H,<sup>201,202</sup> whose acidity level is, of course, lower than those of D points (H > H<sub>D</sub>(RH)).

If the oxidation by H<sup>+</sup> of the light alkanes does not lead to the carbenium ions in superacid media, these cations are produced from the alkyl halides or alkenes by acid-base reactions, according to<sup>216-222</sup>

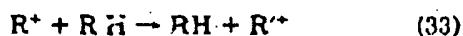


or

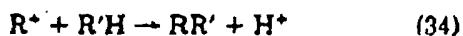


According to the calculated redox potentials (Table V), these carbenium ions are powerful oxidants. Thus, they are used as initiators in isomerization processes<sup>177-179</sup> or as alkylating agents.<sup>219-222</sup> So, with respect to their oxidizing power, they react on alkanes as H<sup>+</sup> ion does,<sup>221,222</sup>

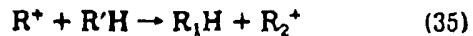
by redox reaction:



by alkylation



by cracking (protolysis reaction):



Following the same procedure as the one presented in section IV, the Gibbs free energies of these basic reactions have been calculated<sup>113</sup> according to the relations

$$\Delta G_{33} = -2F(E^\circ(\text{R}^+/\text{RH}) - E^\circ(\text{R}'^+/\text{R}'\text{H}))$$

$$\Delta G_{34} = -2F(E^\circ(\text{R}^+/\text{RR}') - E^\circ(\text{R}'\text{R}'/\text{R}'\text{H})) + \Delta G_F$$

$$\Delta G_{35} = -F(E^\circ(\text{R}^+/\text{RR}') + E^\circ(\text{R}_2\text{R}_2/\text{R}_2\text{H}) - E^\circ(\text{R}'\text{R}'/\text{R}'\text{H}) - E^\circ(\text{R}_1^+/\text{R}_1\text{R}_1)) + \Delta G_G$$

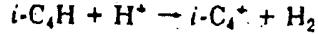
where  $\Delta G_F$  and  $\Delta G_G$  are correction terms (see section IVB).

The most exoenergetic reactions between alkanes and methyl, ethyl, and propyl cations in hydrogen fluoride are reported in Tables XV, XVI, and XVII.

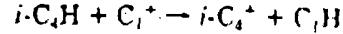
Taking into account the values reported in Table XV, methyl ion appears to be a very high oxidant. Its formation requires highly superacid media, such as HF-SbF<sub>5</sub> or HSO<sub>3</sub>F-SbF<sub>5</sub> mixtures, to yield CH<sub>3</sub>SbF<sub>6</sub> complex.<sup>216-220</sup> Its redox potential is so high that methyl ion reacts on free CH<sub>3</sub>F at room temperature; the principal product is the *tert*-butyl ion i-C<sub>4</sub><sup>+</sup>.<sup>218</sup> The methyl ion is a good alkylating agent,<sup>218-220</sup> but it leads also to redox reactions<sup>220</sup> with alkanes heavier than propane, according to the calculated  $\Delta G$  values. Considering the  $\Delta G$  values reported in Tables XV, XVI, and XVII, a thermodynamic pathway of the methane alkylation by methyl ion is presented in Figure 11. The most exoenergetic reactions are expressed in full lines. The overall process is the sum of three alkylations (eq 33), yielding isobutane, which is oxidized into the stable ion i-C<sub>4</sub><sup>+</sup><sup>218-220</sup> as follows:



Isobutane may be oxidized by H<sup>+</sup> ion or methyl ion, according to



or



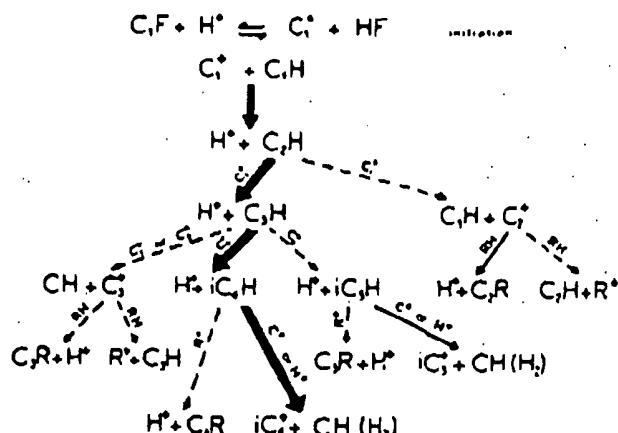


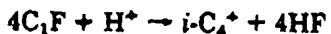
Figure 11. Schematic representation of methane alkylation by methyl fluoride in  $\text{HF-SbF}_5$  or  $\text{HSO}_3\text{F-SbF}_5$  ( $H < -20$ ).

TABLE XVI. Gibbs Free Energies of the Basic Reactions between Ethyl Ion and Alkanes in Hydrogen Fluoride (keal mol<sup>-1</sup>)



alkane, R'H	$\Delta G$	nature of the reaction	$\Delta G$	nature of the reaction
$\text{C}_2\text{H}$	-15	alkylation		
$\text{C}_3\text{H}$	-17	alkylation		
$\text{C}_4\text{H}$	-18	alkylation	-17	redox
$n\text{-C}_4\text{H}$	-18	alkylation	-15	redox
$i\text{-C}_4\text{H}$	-24	redox	-18	alkylation
$n\text{-C}_5\text{H}$	-18	alkylation	-15	redox
$i\text{-C}_5\text{H}$	-25	redox	-17	alkylation
$ne\text{-C}_5\text{H}$	-23	cracking	-16	alkylation
$n\text{-C}_6\text{H}$	-17	alkylation	-16	redox
2MPH	-26	redox	-17	alkylation
3MPH	-25	redox	-17	alkylation
22DMBH	-24	cracking	-20	redox
23DMBH	-26	redox	-24	cracking

Thus, the overall process is equivalent to the self-condensation of methyl fluoride.<sup>218</sup>



or to a single alkylation of methane:

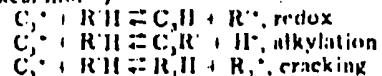


The ethyl cation (Table XVI) presents the same reactivity as that of methyl ion; nevertheless, the reactions are less exoenergetic and the carbenium ion  $\text{C}_2^+$  can be produced in less acidic media, such as  $\text{HF-TaF}_5$ , by dissolving ethene.<sup>166,167</sup> However, the acidity levels of these media are the limit to yield the ethyl ion from ethene because in  $\text{HF-TaF}_5$  (10:1) the alkylation ratio is high,<sup>166</sup> resulting from a quantitative protonation of ethene, while in  $\text{HF-TaF}_5$  (1.5 mol %) the alkylation ratio is low.<sup>167</sup> This is confirmed by the calculated acidity level of ethene protonation (Table VI).

The ethyl ion is still a good alkylating agent.<sup>168,167,220</sup> Its reaction on butanes, for example, in  $\text{HSO}_3\text{F-MF}_3$ <sup>221</sup> or in  $\text{HF-TaF}_5$ ,<sup>168,224,225</sup> leads to the formation of hexanes with good yields. However, as mentioned above for the reactions induced by methyl ion, there is a competition between the basic reactants<sup>220</sup> (Table XVI).

The oxidizing power of the propyl ion is far below the ones of the former carbenium ions, ethyl and methyl cations (Tables V, XVII). However, it is high enough

TABLE XVII. Gibbs Free Energies of the Basic Reactions between Propyl Ion and Alkanes in Hydrogen Fluoride (keal mol<sup>-1</sup>)



alkane, R'H	$\Delta G$	nature of the reaction	$\Delta G$	nature of the reaction
$\text{C}_2\text{H}$	-1	alkylation		
$\text{C}_3\text{H}$	-2	alkylation		
$\text{C}_4\text{H}$	-2	alkylation		
$n\text{-C}_4\text{H}$	-2	alkylation	2	redox
$i\text{-C}_4\text{H}$	-8	redox	-1	alkylation
$n\text{-C}_5\text{H}$	-2	alkylation	1	redox
$i\text{-C}_5\text{H}$	-9	redox	-1	alkylation
$ne\text{-C}_5\text{H}$	-7	cracking	1	alkylation
$n\text{-C}_6\text{H}$	-1	alkylation	1	redox
2MPH	-9	redox	0	alkylation
3MPH	-8	redox	-1	alkylation
22DMBH	-9	cracking	-4	redox
23DMBH	-10	redox	-9	cracking

to initiate isomerization processes<sup>177-179</sup> or to yield alkylation products with low molecular weight alkanes.<sup>221,222</sup> The nearly strong basicity in hydrogen fluoride of propene (Table VI) allows the use of low acidic media to promote the propyl ion formation.

The calculated  $\Delta G$  values of the reactions 33-35 in hydrogen fluoride decrease rapidly when the molecular weight of the involved carbenium ion is increased.<sup>113</sup> The occurrence of any reaction is related to the potential-acidity diagrams of the selected hydrocarbons, which means to the oxidation state. Thus, the alkylation reactions are related to the existence domain of the radical oxidation state (see potential-acidity diagrams); a quantitative alkylation reaction is then observed when the acidity level of the medium is settled in the range D-P of the reagents involved (see next section).

#### D. Alkylations In Low Acidic Media

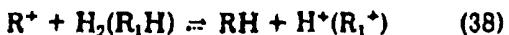
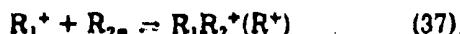
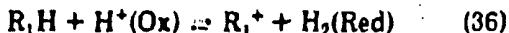
These reactions, so-called "alkene-alkane alkylations", consist of the condensation of an alkane with an alkene, yielding high molecular weight hydrocarbons. These products present high octane numbers and are of great interest for the synthesis of motor fuels. Thus, a great number of alkylation processes has been reported in the literature during the last decade.

The selected alkanes generally are butanes, but also pentanes or hexanes, and the chosen alkenes are mainly propene or isobutene, and occasionally butenes or pentenes. The reactions are carried out in low acidic media vs. the superacid media such as  $\text{HF-SbF}_5$ . The selected media are neat Brønsted acids or mixtures:  $\text{HF}$ ,<sup>226-231</sup>  $\text{HF-HSO}_3\text{H}$ ,<sup>232</sup>  $\text{HF-CF}_3\text{SO}_3\text{H}$ ,<sup>233</sup>  $\text{HF-H}_2\text{S-O}_4$ ,<sup>234</sup>  $\text{HSO}_3\text{F}$ ,<sup>235</sup>  $\text{FSO}_3\text{H-H}_2\text{SO}_4$ ,<sup>236,237</sup> or  $\text{CF}_3\text{SO}_3\text{H-H}_2\text{SO}_4$ .<sup>238,239</sup> Taking into account the general acidity scale (Figure 3) and the basic nature of alkenes, the acidity levels of these media are lower than that of pure sulfuric acid, which means  $H > -12$ .

Two basic processes have been suggested for the understanding of these alkylation reactions: the alcoylation reaction on one hand, and the alcoyolysis on the other hand.

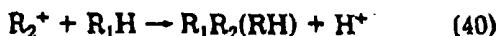
The alcoylation reaction results from the acid-base reaction between an alkene and an alkylcarbenium ion.<sup>171,167-169</sup> The carbenium ion is produced by oxidation of the parent alkane; the overall process is represented by eq 36-38.

## Thermodynamic Behavior of Alkanes



According to eq 36-38, the process involves the oxidation of  $R_1H$  into the carbenium ion and the condensation of  $R_1^+$  with the alkene  $R_{2-}$ , the reverse of  $\beta$  scission (section IVB). In fact, allowing for the potential-acidity diagrams of alkanes, the acidity level of the media is too low for a direct oxidation of alkane  $R_1H$  into the carbenium ion:  $H > H_D(R_1H)$ . Furthermore, considering the basic nature of alkenes (Table VI), the alkene (generally propene or isobutene) is protonated. Thus, the alcoyolysis reaction does not appear satisfactory.

The alcoyolysis reaction is similar to the condensation reaction 14 and results from the oxidation of an alkane by a carbenium ion.<sup>172,173,221,222</sup> This reaction is then related to the basic nature of alkene, and the overall process is represented by the reactions



The redox reaction 40 is the sum of the electrochemical reactions

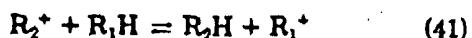


Therefore,  $\Delta G_{40}$  is related to the standard potentials of the redox couples  $R_2^+/R_2R_2$  and  $R_1R_1/R_1H$ , which means the radical oxidation state domain. Then, taking into account the potential-acidity diagrams of alkanes, the  $H_D$  values (Table IX) and the  $H_p$  values (Table VI), the necessary conditions of occurrence of the alkylation reaction are as follows: the acidity level of the medium has to be higher than that of alkene protonation, meaning that  $H < H_p(R_{2-})$ ; the acidity level of the medium has to be lower than that of the radical dismutation, which means that  $H > H_D(R_1H)$  and  $H > H_D(R_2H)$ .

In short, the alkylation conditions are  $H_D(R_1H) < H < H_p(R_{2-})$ .

In the isobutene-butanes alkylation processes, the alkylation conditions are expressed by  $-16.4 < H < -6.3$ , which is in good agreement with the acidity levels of the media used for this alkylation process ( $H \sim -12, -10$ ).

In contrast, if the acidity level is much too high ( $H < H_D$ ), the alkylation does not take place. The redox exchange may occur, depending on the standard potentials of the redox couples  $R_2^+/R_2H$  and  $R_1^+/R_1H$ , as follows:



Such reactions occur in alkylation processes involving ethene or methyl fluoride<sup>220</sup> (section Vc) because the acidity of the solvent has to be high enough to yield the carbenium ion, but it is too high, with respect to the  $H_D$  value of the alkane, to be alkylated. Furthermore, if the acidity level is much too low ( $H > H_p(R_{2-})$ ), the

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alkene is not protonated and then cannot oxidize the alkane; no reaction takes place.

## VI. Conclusion

Thermodynamics appear to be a good tool for the description of the reactivity of alkanes in various superacid media. The potential-acidity diagram (Pourbaix's type) represents the variations of the potentials of the alkane redox couples as a function of the acidity level. Its use is quite simple and provides a rational understanding of the occurrence of the basic processes in any superacid media. One of the most important characteristics of the diagram is the disproportionation of the radical oxidation state:  $H_D$ . According to the  $H_D$  values of alkanes, the medium may be chosen in order to enhance or inhibit any kind of reaction: simple cationic isomerization of alkanes occurs at acidity levels higher than the disproportionation ones of the corresponding radical oxidation states, which means that  $H < H_D(RH)$ ; condensation or alkylation reactions are observed at acidity levels lower than the disproportionation ones of the radical oxidation state of the selected hydrocarbons, meaning that  $H > H_D(RH)$ .

Nevertheless, such diagrams are based on the approximations of the thermochemical properties of alkane redox couples in superacid media. Therefore, the determination of these values is an open field for the future. However, the uncertainties are not very large: for light alkanes, the errors in the evaluation of Gibbs free energies are lower than 10 kcal mol<sup>-1</sup> while they are reduced to a few tenths kcal mol<sup>-1</sup> for tertiary alkanes.<sup>25</sup> Thus, the reactivity of an alkane may be well defined among the basic reactions, according to the acidity level of the solvent. The validity of the reactivity model described has been checked through the examples discussed in section V. By following the procedure presented in this review, the previsions are easily widened to any case.

In addition to the thermodynamic analysis, the kinetic parameters cannot be forgotten. The reactions described constitute the initial steps of complex pathways. The condensation products are indeed more reactive than the initial compounds, and their reactivities are then described according to their thermochemical properties. Thus, kinetic and thermochemical data must be collected in order to reach a complete description of the chemical behavior of alkanes in superacid media. However, the framework presented here provides a trial of rationalization and a new point of view on the chemistry of alkanes in superacid media.

## VII. Acknowledgments

We thank our co-workers, Dr. Ben Hadid, P. Capron, and F. Bedioui. They deserve the credit for the experiments from our research group that have contributed to the field of investigations of nonaqueous solvents. Several people have helped us enter the chemistry of alkanes in superacid media. In particular, we are grateful to Professor A. Commeiras, Dr. A. Germain, and Dr. D. Blin of U.S.T.L. (Université de Montpellier, France), Dr. J. M. Bourguignon of the University of Strasbourg, and Dr. B. Torck (Institut Français du Pétrole, Rueil-Malmaison, France) for continuing helpful discussions. The "Délégation Générale de la

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